# JOURNAL

OF

# THE CHEMICAL SOCIETY.

---

## ABSTRACTS OF PAPERS

ON

## PHYSICAL, INORGANIC, MINERALOGICAL, PHYSIOLOGICAL, AGRICULTURAL,

AND

## ANALYTICAL CHEMISTRY.



**Committee of Publication:**

H. E. Armstrong, Ph.D., F.R.S.
J. Dewar, LL.D., F.R.S.
Wyndham R. Dunstan, M.A., F.R.S.
A. Vernon Harcourt, M.A., F.R.S.
R. Meldola, F.R.S.
W. Ramsay, Ph.D., F.R.S.
W. J. Russell, Ph.D., F.R.S.
J. Millar Thomson, F.R.S.
T. E. Thorpe, LL.D., F.R.S.
W. A. Tilden, D.Sc., F.R.S.
W. P. Wynne, D.Sc., F.R.S.

**Editor:**

C. E. Groves, F.R.S.

**Sub-editor:**

A. J. Greenaway.

**Abstractors:**

C. F. Baker, Ph.D., B.Sc.
A. G. Bloxam.
C. H. Bothamley.
A. C. Chapman.
H. Crompton.
A. W. Crossley, M.Sc., Ph.D.
T. Ewan, B.Sc., Ph.D.
M. O. Forster, Ph.D.
W. D. Halliburton, M.D., B.Sc., F.R.S.
A. Harden, M.Sc., Ph.D.
L. M. Jones, B.Sc.
L. De Koningh.
A. Lapworth, D.Sc.
A. R. Ling.
D A. Louis.
N. H. J. Miller, Ph.D.
W. J. Pope.
E. C. Rossiter.
R. Routledge, B.Sc.
M. J. Salter.
L. J. Spencer, M.A.
J. J. Sudborough, Ph.D., D.Sc.
J. F. Thorpe, Ph.D.
M. W. Travers.
E. W. Wheelwright, B.A., Ph.D.



---

**1897. Vol. LXXII. Part II.**

---

LONDON:
GURNEY & JACKSON, 1, PATERNOSTER ROW.
1897.

# JOURNAL

OF

# THE CHEMICAL SOCIETY.

## ABSTRACTS OF PAPERS

ON

## PHYSICAL, INORGANIC, MINERALOGICAL, PHYSIOLOGICAL, AGRICULTURAL,

AND

## ANALYTICAL CHEMISTRY.







1897. Vol. LXXII. Part II.

LONDON:
GURNEY & JACKSON, 1, PATERNOSTER ROW.
1897.

Richard Clay and Sons, Limited,
london and bungay.

# CONTENTS.

## ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS :—

## PART II.

### *General and Physical Chemistry.*

## *Inorganic Chemistry.*

## *Mineralogical Chemistry.*

## *Physiological Chemistry.*

## *Chemistry of Vegetable Physiology and Agriculture.*

## *Analytical Chemistry.*

JOURNAL

OF

# THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART II.

## General and Physical Chemistry.

**Indices of Refraction of Metals at different Temperatures** By A. PFLÜGER (*Ann. Phys. Chem.*, 1896 [2], **58**, 493—499).—Kundt, who determined the indices of refraction of a number of metals at different temperatures (Abstr., 1889, 749), came to the conclusion that the temperature coefficients for the indices of refraction are of the same order as the coefficients of the electrical conductivities of the metals, and that, therefore, the velocity of light at different temperatures in a given metal is directly proportional to the electrical conductivity. As this result is not in harmony with recent observations of the reflection of metals at different temperatures, the author has been led to repeat some of Kundt's determinations, using the metallic prisms formerly employed. The results obtained are not in agreement with those of Kundt, and are not found to support his conclusions with reference to the velocity of light and the electrical conductivity in metals. H. C.

**Refractometric Researches.** By JOHAN F. EIJKMAN (*Rec. Trav. Chim.*, 1896, **15**, 52—60).—The author calculates the molecular refractions for a number of the hydrocarbons of the paraffin series, making use of the formula which he has given in a previous paper $MV(n^2-1)/(n+0{\cdot}4)$. The change in the refraction and dispersion for every additional $CH_2$ group is constant from the sixth term, the values being for the lines $H\beta$, $H\alpha$, and A.

$\beta = 10{\cdot}431$ $\alpha = 10{\cdot}260$ $A = 10{\cdot}052$ $\beta - \alpha = 0{\cdot}171$

These numbers are independent of the temperature, and correct to within one unit of the third decimal. The calculated values for the two methyl groups or hydrogen atoms at the ends of the chain are then

| | $\beta$ | $a$ | A | $\beta - a$ |
|---|---|---|---|---|
| $CH_3$ | 12·285 | 12·105 | 11·885 | 0·180 |
| $H_2$ | 3·71 | 3·69 | 3·67 | 0·020 |

H. C.

**Behaviour of Circularly Polarising Crystals in a State of Powder.** By Hans Heinrich Landolt. (*Ber.*, 1896, **29**, 2404—2412).—The specific rotation of isotropic circularly polarising crystalline substances may be determined in an ordinary polarimeter tube by suspending the finely-powdered material in a liquid of its own refractive index and measuring the angle through which the polarisation plane of the entering beam is deflected; the material is powdered in an agate mortar and sifted, the particles being preferably of 0·004—0·012 m.m. in diameter. The polarimeter tube should be rotated whilst the measurements are made in order to keep the powder in homogeneous suspension; the rotation may be either right or left-handed, but the number of revolutions per minute should be 50—80, because at higher speeds the solid particles are driven to the sides of the tube by centrifugal force and the readings thus made valueless. Several series of experiments were made with right and left-handed sodium chlorate, the powder being placed in a test tube with alcohol, and carbon bisulphide slowly added until the mixture was as transparent as possible; the mixture was then transferred to the polarimeter tube and, after the reading had been taken, the contents of the tube were evaporated to dryness in order to determine the weight of salt employed. The specific rotation of sodium chlorate was in this way determined as $[a]_j = \pm 1·42°$ per m.m., practically the same value as is obtained with plates of the massive salt; it is thus evident that particles of sodium chlorate of 0·004—0·012 m.m. in diameter still possess the same crystalline structure as that to which the circular polarisation of the large crystals is due. W. J. P.

**The Characteristics of Optically Isomeric Compounds.** By Hermann Traube (*Ber.*, 1896, **29**, 2446—2447). Walden (Abstr., 1896, 553) has brought forward a number of substances which do not conform to Pasteur's rule that all substances which are optically active in solution crystallise in hemihedral forms. It must, however, be remembered that the crystallographic symmetry of none of these has been completely investigated. In most cases, the form has simply been determined, but no attempt has been made to ascertain the exact degree of symmetry of the crystal by the study of etch figures, the pyro-electric properties, etc. In every case which has thus been carefully examined, Pasteur's law has been verified. The same remarks apply to the exceptions to the rule that the crystal forms of two oppositely active modifications of a substance are enantiomorphous.

The author further points out that Becke (*Tschermak's Min. und*

*petrogr. Mitthlg.* 1889, **10**, 414; 1891, **12**, 256) has shown that Pasteur's rule can be directly deduced from the Le Bell-van't Hoff theory.

A. H.

**Influence of Linking on the Rotatory Power.** By PAUL WALDEN (*Zeits. physikal. Chem.*, 1896, **20**, 569—585).—A number of compounds were investigated to determine the relations between the optical properties of saturated and unsaturated compounds in both the aliphatic and aromatic series. The experimental results are given in the accompanying table, in which $V$ = the molecular volume, $R$ is the molecular refraction (Lorenz) observed, and $R_{(calc)}$ that calculated from Conrady's numbers, $D$ is the molecular dispersion $(n_f - n_c) M/_d$; $[M]$ the molecular rotation and $S$ the difference in the latter for $- H_2$.

| | $V$ | $R$ | $R_{calc}$ | $D$ | $[M]$ | $S$ |
|---|---|---|---|---|---|---|
| Amylic butyrate | 181·82 | 45·41 | 45·39 | 1·153 | + 4·33° | 2·29° |
| Amylic crotonate | 174·15 | 45·62 | 45·00 | 1·69 | + 6·62° | |
| Amylic isobutyrate | 183·32 | 45·42 | 45·39 | 1·151 | + 4·90° | ·57° |
| Amylic methylacrylate | 177·66 | 45·24 | 45·00 | 1·524 | + 5·47° | |
| Amylic succinate | 268·98 | 70·04 | 70·28 | 1·926 | + 9·71° | 5·46° |
| Amylic fumarate | 264·03 | 70·89 | 69·89 | 2·487 | +15·17° | |
| Amylic chlorosuccinate | 283·6 | 75·27 | 75·23 | 2·178 | +10·98° | 5·80° |
| Amylic chlorofumarate | 275·1 | 75·53 | 74·83 | 2·636 | +16·78° | |
| Amylic methylsuccinate | 285·5 | 74·53 | 74·88 | 2·31 | + 9·99° | 6·02° |
| Amylic mesaconate | 278·47 | 75·52 | 74·47 | 2·76 | +16·01° | |
| Amylic tricarballylate | 387·05 | 103·1 | 104·3 | 2·69 | +15·48° | 8·18° |
| Amylic aconitate | 382·90 | 104·32 | 103·97 | 3·50 | +23·66° | |
| Amylic phenylpropionate | 226·32 | 65·07 | 65·13 | 2·603 | + 4·98° | 11·38° |
| Amylic cinnamate | 218·2 | 68·30 | 64·73 | 5·106 | +16·36° | |
| Amylic phenylpropiolate | 215·35 | 66·79 | 63·32 | 4·33 | +12·05° | |
| Amylic α-naphthoate | 228·19 | 74·55 | 71·44 | 5·43 | +12·78° | 9·83° |
| Amylic β-naphthoate | 229·8 | 75·20 | 71·44 | 5·52 | +22·61° | |

From the above results, the author draws these conclusions:—The influence of the double linking as compared with the single linking is to cause:—(1) an increase in the density, and hence a decrease in the molecular volume; (2) an abnormal molecular refraction which is not only greater than the calculated value, but also greater than that of the allied singly linked compound; (3) a marked increase in the molecular dispersion and a great increase in the molecular rotation. The influence of the triple linking is similar to that of the double linking, but less marked. The naphthalene derivatives show anomalies in their optical properties, the rotation of the β-derivative being extraordinarily great.

L. M. J.

**Luminescence.** By W. ARNOLD (*Zeits. Kryst. Min.*, 1896, **27**, 92—93).—The phosphorescence observed by Pope (*Trans.*, 1895, **67**, 985) on crushing crystals of orthobenzoicsulphinide is termed tribo-luminescence in accordance with Wiedemann's suggestion.

The author has examined saligenin, benzophenone, benzoic acid

salicylic acid, gallic acid, tannin, hippuric acid, and vanillin for cathodoluminescence, thermoluminescence, and triboluminescence; hippuric acid, however, is the only one which shows triboluminescence. Orthobenzoicsulphinide shows no cathodoluminescence, and its triboluminescence is less marked than that of hippuric acid.

None of the substances named above show fluorescence on exposure to Röntgen rays, but are all quite transparent to them.

W. J. P.

**Santonin and its Derivatives.** By LUIGI BRUGNATELLI (*Zeits. Kryst. Min.*, 1896, **27**, 78—90. Compare Andreocci, this vol., i, 182).—The etch-figures produced by alcohol, ether, or ethylic acetate on rhombic crystals of optically active santonin indicate that the crystals are hemihedral.

On crushing crystals of ethylisodesmotroposantonin, a yellow phosphorescence is observed; similarly, crystals of dextro- and lævo-ethylic santonite and lævodesmotroposantonous acid exhibit a yellowish green phosphorescence, whilst crystals of lævoethyldesmotroposantonous acid show an emerald green phosphorescence on being crushed. The phosphorescence is of a similar kind to that observed by Pope on breaking crystals of orthobenzoicsulphinide (*Trans.*, 1895, **67**, 985).

No connection seems to exist between phosphorescence of this kind and optical activity, although the phenomenon is not observed with the racemic modifications of the substances mentioned above; a connection may possibly exist between the cleavage and the phosphorescence, since several substances exhibiting a good cleavage phosphoresce on trituration. Many substances, however, like phenacetin, which possess a good cleavage, do not phosphoresce, whilst others, which have no cleavage, like dichloromethylparatolylsulphone, show the phenomenon well.

W. J. P.

**Theory of Liquid Chains.** By JOHAN M. LOVÉN (*Zeits. physikal. Chem.*, 1896, **20**, 593—600).—The difference of potential between two solutions was investigated for the case in which the anions are similar but the cations respectively univalent and bivalent. The equation obtained is

$$\pi_1 - \pi_2 = 0{\cdot}002\,T.\frac{3u_1 - 2u_2 + v}{3u_1 - 4u_2 - v}\log\frac{3\,(u_1 + v)}{4\,(u_2 + v)}$$

where $u_1$ and $u_2$ are the migration velocities of the univalent and bivalent cations, and $v$ that of the anion. To test the validity of the expression, the E.M.F. was determined in the case of chains containing hydrogen chloride and chloride of barium, calcium, magnesium or zinc. In dilute solutions ($C_1 = 0{\cdot}01$), the agreement is satisfactory, but in more concentrated solutions ($C_1 = 0{\cdot}1$) the agreement is not good, probably owing to incomplete dissociation.

L. M. J.

**Peroxide Electrodes.** By OLIN F. TOWER (*Zeits. physikal. Chem.*, 1896, 21, 90—92).—Owing to an erroneous calculation, the values given in some of the tables of the author's previous paper (Abstr., 1896, ii, 142) are wrong. The corrected values are given in this paper, and when these corrections are made, it is seen that the values

for the hydrogen dissociation in acid organic salts obtained by the author do not agree with those of Trevor as previously stated.

L. M. J.

**Peroxide Electrodes.** By W. A. SMITH (*Zeits. physikal. Chem.*, 1896, **21**, 93—107).—The author gives a short account of points in the preparation of the electrodes wherein he differs from Tower (Abstr., 1896, ii, 142). He finds also that, with many acids, constant values for the E.M.F. are not obtainable. In those acids which yield a constant E.M.F., the values for the dissociation calculated from the expression $\pi = 0{\cdot}02908 . \log m^4c^4/m'^4,c'^4$, do not agree with those obtained by other observers. Replacing the exponent 4 by a variable, $x$, and calculating back from the dissociation, values varying between 3·4 and 3·7 are obtained, but they are approximately constant for each of the acids and its salts. Hence by the use of the mean value 3·56 in place of 4, results are obtained in better accord with the dissociation. This, however, is probably only approximate, for the value varies with the acid ion; being however equal for the acid and the salt, it may be first obtained from the acid and then the hydrogen dissociation calculated for the acid salts. By this means, values are obtained in better accord with theoretical considerations and with the results of other observers than are those of Tower.

L. M. J.

**Electrolytic Behaviour of Solutions of Salts and Acids in Methylic Alcohol.** By NICOLAI D. ZELINSKY and SERGEI G. KRAPIWIN (*Zeits. physikal. Chem.*, 1896, **21**, 35—52).—The authors determined the conductivity of a number of salts and acids in aqueous solution, and in methylic alcohol, employing Ostwald's modification of Kohlrausch's method. The bromides and iodides of potassium and ammonium behave in the alcoholic solution as strong electrolytes, the conductivity at $v = 512$ being only about 30 per cent. less than that in aqueous solution. Cadmium iodide has a very small alcoholic conductivity, the ratio, $mv_2/mv_1$ increasing with dilution. In the substituted ammonium compounds, such as tetramethylammonium bromide and iodide, tetrethylammonium iodide, ethylmenthylamine hydrochloride and nitrate, the conductivity differed only slightly in the two solvents. Ethylenediamine hydrochloride is also fairly strongly dissociated in alcohol. Hydroxylamine hydrochloride exhibits, in aqueous solution, a rapid increase of the value $mv_2/mv_1$ owing to decomposition of the compound into acid and base, but this does not occur in the alcoholic solution. Tin diethyl- and triethyl-iodides behave in alcohol as weak electrolytes and obey the dilution law; the addition of water to the former markedly raises the conductivity, probably owing to decomposition. It is noticeable that oxalic and iodic acids behave also as very weak electrolytes. In dimethylsuccinic acid, the conductivity is found to be almost proportional to the volume. (Comp. Trevor, Abstr. 1893, ii, 62), whilst trichloracetic acid is found to obey the dilution law in methylic alcohol, a result previously obtained for ethylic alcohol by Wildermann (Abstr. 1894, ii, 375). The addition of water, not only in small but also in large quantities, diminishes the conductivity of the alcoholic solutions of alkali bromides, &c. Thus

the solution containing 50 per cent. of water has a conductivity about 0·7 of that in alcohol and about 0·5 of that in water. L. M. J.

**Melting Points of Aluminium, Silver, Gold, Copper and Platinum.** By SILAS W. HOLMAN, R. R. LAWRENCE and L. BARR (*Phil. Mag.*, 1896 [5], **42**, 37—51).—With the help of a platinum and rhodo-platinum thermo-couple, the authors have determined the melting points of a number of pure metals. With the exception of the platinum, the metals used were all of a high degree of fineness. The absolute values obtained depend in part on the assumption of 1072° as the melting point of pure gold (Holborn and Wien, Abstr., 1896, ii, 87). The numbers are offered as provisional only, but with the belief that they are more trustworthy than previous data.

| | | | |
|---|---|---|---|
| Aluminium | 660° | Copper | 1095° |
| Silver | 970° | Platinum | 1760° |

H. C.

**Determination of Specific Heats by means of the Electric Current.** By A. SCHLAMP (*Ann. Phys. Chem.*, 1896, [2], **58**, 759—770).—Pfaundler has shown that if a current is sent through the resistances $\omega_1$ and $\omega_2$ placed in calorimeters which contain the quantities $m_1$ and $m_2$ of liquids of the specific heats $c_1$ and $c_2$,

$$\frac{m_1 c_1 \Delta t_1 + r_1 \Delta t_1}{m_2 c_2 \Delta t_2 + r_2 \Delta t_2} = \frac{\omega_1}{\omega_2}$$

where $r_1$ and $r_2$ are the water equivalents of the vessels, stirrers, &c. and $\Delta t_1$ and $\Delta t_2$ are the corrected rises in temperature. In using this method for specific heat determinations, the specific heat of one of the liquids used must be known and that of the other can then be calculated.

The author has determined the specific heats of the following substances in the liquid state at temperatures above 90°, the specific heat of turpentine being deduced from Regnault's determination and used as the standard of reference.

| | Sp. Heat. | Temperature. | Mol. Heat. |
|---|---|---|---|
| Turpentine | 0·5055 | 93° | — |
| Nitrobenzene | 0·4023 | 93 | 49·48 |
| Aniline | 0·5378 | 92·5 | 50·03 |
| Benzene | 0·4814 | 94 | 37·55 |
| Naphthalene | 0·4272 | 94·5 | 54·68 |
| α-Naphthylamine | 0·4756 | 94·2 | 68·01 |
| Nitronaphthalene | 0·3900 | 94·3 | 67·47 |
| Paratoluidine | 0·5335 | 94·1 | 57·05 |
| Phenol | 0·5610 | 93·9 | 52·73 |
| Orthotoluidine | 0·5364 | 94·0 | 57·40 |

H. C.

**Specific Heat of Viscous Sulphur.** By J. DUSSY (*Compt. rend.*, 1896, **123**, 305—308).—Sulphur contained in a thin glass bulb was heated to the desired temperature, and the bulb was then lowered into a thin glass tube of somewhat greater diameter contained in the calorimeter, and allowed to cool under these conditions. In some of the experiments, after the temperature had fallen below 157°, the

bulb containing the sulphur was broken, and the contents allowed to mix with the water. These precautions were taken in order to prevent the formation of plastic sulphur in an indefinite condition. The following results were obtained.

| Temperature | 160–201° | 160–232·8° | 160–264° | 201–232·8° | 232·8–264° |
|---|---|---|---|---|---|
| Mean specific heat | 0·279 | 0·300 | 0·300 | 0·331 | 0·324 |

The curve representing the loss of heat between a given temperature T and 0° seems to change in direction at about 230°.

*Vitreous Sulphur.*—When tempered between 157° and 175°, sulphur solidifies very rapidly, and has a characteristic vitreous appearance. Sulphur heated to 220°, poured suddenly into cold water, and allowed to cool in contact with it, yields an outer layer of plastic sulphur, an intermediate layer of vitreous sulphur, and an inner core of the prismatic variety. This vitreous form seems to be the analogue of the well-known vitreous selenium. C. H. B.

**Specific Heats at Constant Volume of the $C_nH_{n2+2}$ Hydrocarbons.** By ADOLFO BARTOLI and ENRICO STRACCIATI (*Gazzetta*, 1896, **26**, i, 472—474).—The determination of the coefficients of compressibility, $K_t$ (this vol. ii, 9), renders it now possible to calculate the specific heats, $C$, at constant volume of these hydrocarbons by Thomson's formula—

$$c = C - \frac{10336\, T (v_o \delta_t)^2}{E\, K_t\, v_t},$$

in which $C$ is the specific heat at constant pressure, $v_t$ the specific volume at the temperature $t = 23°$, $T$ the absolute temperature $273° + t°$, $\delta_t$ the coefficient of thermal expansion and $E$ the mechanical equivalent of heat. The principal values concerned, namely, $c$, $C$ and $C/c$, are tabulated in the abstract referred to. The authors conclude that whilst the specific heats at constant pressure of the $C_nH_{2n+2}$ hydrocarbons are practically the same, the specific heats at constant volume increase as the molecular weight rises; the ratio $C/c$ of the two specific heats increases regularly as the molecular weight decreases, but never attains the value 1·41 which the ratio has in the case of gases.

W. J. P.

**Selection of the Unit of Heat.** By ADOLFO BARTOLI (*Gazzetta*, 1896, **26**, i, 475—482).—The author discusses the various units of heat in use, and concludes that it would be most convenient to define the thermal unit as the quantity of heat necessary to raise the temperature of 1 kilo. of water at 15° by 1° of the normal nitrogen thermometer of the *Sèvres bureau international des poids et mesures.*

W. J. P.

**Cyanic Acid.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1896, **123**, 337—341).—When a strong acid is added to an alkali cyanate the first thermal disturbance is due to the displacement of the cyanic acid, but this is followed by a further disturbance due to transformations of the liberated cyanic acid.

With acetic acid and potassium cyanate, the early development of heat amounts to 1·05 Cal., and it follows that the heat of neutralisation of cyanic acid is + 12·25 Cal. With hydrochloric acid, the results are less distinct, owing to the rapid transformation of the cyanic acid, but they tend to confirm that obtained with acetic acid. Boric acid gives no thermal disturbance, and this also indicates that the heat of neutralisation of cyanic acid is about 12·0 Cal. Adopting 12·25 Cal. as the heat of neutralisation, it follows that

$$C + N + H + O + Aq. = HCNO \text{ diss. develops} + 37{\cdot}0 \text{ Cal.}$$
$$HCN \text{ diss.} + O = HCNO \text{ diss.} \quad + 61{\cdot}4 \text{ Cal.}$$

The conversion of cyanic acid into ammonium hydrogen carbonate develops + 24·0 Cal.

The addition of ammonium chloride to potassium cyanate solution absorbs − 0·2 Cal., and it follows that the heat of neutralisation of cyanic acid by ammonia is about + 10·7 Cal. The heat of formation of ammonium cyanate from its elements is + 68·9 Cal., and the conversion of dissolved ammonium cyanate into carbamide will develop 8·3 Cal. C. H. B.

**Thermodynamical Surfaces of a Substance in the Solid and Liquid States.** By GUSTAV TAMMANN (*Zeits. physikal. Chem.*, 1896, **21**, 17—34).—In an ordinary thermodynamical surface, a break occurs at the change from liquid to solid state. The effect is considered of employing in place of the parameter $p$ the value for the actual internal pressure $p+k$, and calculations are made on the assumption that this would give one thermodynamical surface without breaks. The relation $(dv'/dp)>(dv''/dp)$ is deduced (where $v'$ refers to solid and $v''$ to liquid), and this is in accord with the experiments of Barus on the compressibility of solid and liquid naphthalene. The inequality $(dv'/dT)>(dv''/dT)$ is also obtained, a result which is also proved by the experimental evidence available. The continuity of the surface cannot, however, be assumed in case of such compounds as wax, alloys, &c., which have no definite melting-point, or in which two or more classes of molecular groups exist. The paper concludes with a discussion of the forms of the curve representing melting point/pressure in different classes of compounds, a maximum occurring in these cases where $v'>v''$ and a minimum also if $v'<v''$. L. M. J.

**Specific Gravities of Mixtures of Normal Liquids.** By CHARLES E. LINEBARGER (*Amer. Chem. J.*, 1896, **18**, 429—453).—The author terms those liquids "normal," which, as indicated by the work of Guye, Ramsay and Shields, and others, are formed from their vapours without any change in molecular condition. If the degree of molecular association of liquids be taken as a basis of classification, three classes of binary mixtures may be distinguished.

1. The liquids mixed are normal;
2. One liquid is normal, the other associated;
3. Both liquids are associated.

Mixtures of the first class may be expected to exhibit the simplest behaviour in respect to their physical properties, and as the mixing of

normal liquids is not attended by any change in the number of molecules present, it becomes of interest to inquire what changes of volume occur when such liquids are mixed. For this purpose, the densities of a number of binary mixtures of normal liquids have been determined with all possible care. The liquids chosen were benzene, toluene, chlorobenzene, nitrobenzene, ether, ethylic acetate, ethylic iodide, ethylic benzoate, carbon bisulphide, chloroform, carbon tetrachloride, and turpentine. The mixtures were in all cases found to have a volume differing slightly from the sum of the volumes of the components, so that there is generally either a contraction or expansion in volume when two normal liquids are mixed. The author attributes this behaviour on the one hand to specific actions between the molecules of the liquids mixed, and on the other hand to the reduction of the internal pressure which attends the dilution of one liquid by another. H. C.

**Compressibility Coefficients of the $C_nH_{2n+2}$ Hydrocarbons.** By ADOLFO BARTOLI (*Gazzetta*, 1896, **26**, i, 466—471).—The author has determined the compressibility coefficients $K_t$, at a temperature $t = 23°$, of a series of paraffinoid hydrocarbons obtained by fractionating Pennsylvanian petroleum, using a piezometer of the type described by Guillaume (*Études thermometriques*, p. 28). The results are given in the following table, together with the boiling-points, $B$, and the densities at 0°, $d_0$, of the hydrocarbons :—

| | $B$ | $d_0$ | $K_t$ | $C$ | $c$ | $C/c$ |
|---|---|---|---|---|---|---|
| $C_6H_{14}$ | 68° | 0·6950 | 0·0001592 | 0·5042 | 0·3719 | 1·355 |
| $C_7H_{16}$ | 93 | 0·7328 | 0·0001341 | 0·4842 | 0·3776 | 1·282 |
| $C_8H_{18}$ | 117 | 0·7463 | 0·0001214 | 0·5111 | 0·4084 | 1·251 |
| $C_9H_{20}$ | 137 | 0·7624 | 0·0001125 | 0·5015 | 0·4003 | 1·252 |
| $C_{10}H_{22}$ | 160 | 0·7711 | 0·0001054 | 0·5058 | 0·4065 | 1·244 |
| $C_{11}H_{24}$ | 181 | 0·7817 | 0·0000974 | 0·5032 | 0·4069 | 1·236 |
| $C_{12}H_{26}$ | 199 | 0·7915 | 0·0000917 | 0·5065 | 0·4102 | 1·234 |
| $C_{13}H_{28}$ | 219 | 0·8017 | 0·0000874 | 0·4987 | 0·4039 | 1·233 |
| $C_{14}H_{30}$ | 238 | 0·8130 | 0·0000827 | 0·4997 | 0·4090 | 1.221 |
| $C_{15}H_{32}$ | 260 | 0·8224 | 0·0000787 | 0·4991 | 0·4099 | 1·217 |
| $C_{16}H_{34}$ | 280 | 0·8287 | 0·0000754 | 0·4964 | 0·4142 | 1·198 |

W. J. P.

**Capillary Behaviour of the Crystal Faces of Rock-salt and Sylvine towards the Mother Liquors.** By ST. BARENT (*Zeits. Kryst. Min.*, 1896, **26**, 529—557).—Curie, Sohncke, Bravais, and others have shown theoretically that the particular forms occurring on a crystal are determined by the number of mass-points or molecules lying in unit area of the faces of those forms, which number is, in turn, intimately connected with the capillarity constant. The capillarity constant should be the same in all faces of the same form, but different for faces of different forms; the form the faces of which are most thickly studded with mass-points should be that developed

most frequently during the crystallisation of any particular substance, and should have a smaller capillarity constant than any other possible form on the crystal. The capillarity, measured between a crystal face and the mother liquor surrounding it, is, however, not conditioned solely by the crystalline structure but also by the nature of the mother liquor, the temperature, pressure, &c.; the different habits of the crystals of a substance which can be developed by crystallisation from different solvents and at different temperatures are thus due to changes in capillarity.

These apparently sound views not having yet been put to adequate experimental test, the author has made series of capillarity determinations with differently orientated plates of rock-salt and sylvine; the determinations made by Quincke's method of measuring the bordering angle (Randwinkel) between liquid and solid are in concordance with the theory.

The experiments made with rock-salt and its saturated aqueous solution show that crystallographically different crystal faces have a different capillary behaviour towards the same mother liquor; the mother liquor makes a smaller bordering angle with a crystalline face, the more thickly the latter is studded with mass-points. The bordering angles are, for rock-salt and its saturated aqueous solution, of the order 7·5° for the form {100}, 8·7° for {110}, 13·5° for {111}, and 11·1° for {210}, but on adding carbamide to the saturated mother liquor, the bordering angle on the form {100} increases, whilst that on {111} decreases, so that the latter angle becomes less than the former when the mother liquor contains a certain percentage of carbamide; the reason is thus given of the well-known curious fact, that whilst sodium chloride crystallises in cubes from a pure aqueou solution, it separates in octahedra from urine or an aqueous solution containing carbamide. The addition of caustic soda, chromic chloride, or potassium hydrogen oxalate to sodium chloride solution also causes the crystals formed to become octahedra, and in each of these cases the author finds that the bordering angle on the octahedron is less than that on the cube form. The addition of sodium carbonate, which does not alter the forms present of the sodium chloride crystals, was found not to reverse the order of magnitude of the bordering angles on the forms {100} and {111}. W. J. P.

**Coefficients of Division of Phosphoric Acid between Ether and Water.** By MARCELLIN BERTHELOT and GUSTAVE ANDRÉ (*Compt. rend.*, 1896, **123**, 344—349).—Ether free from alcohol and saturated with water was shaken with definite volumes of phosphoric acid solutions of various strengths, and the quantity of phosphoric acid in the ether and water respectively was determined by titration. With a solution of phosphoric acid in about 11 times its weight of water, it was found that 1 c.c. of water contained 0·0886 gram of phosphoric acid, whilst 1 c.c. of ether contained only 0·000033 gram, the coefficient of division being $\frac{1}{2700}$. With acid five times more concentrated, the coefficient was $\frac{1}{2900}$, whilst with a solution containing 0·434 gram of phosphoric acid per c.c. the quantity dissolved by the ether was infinitesimal. On the other hand, when ether containing a considerable quantity of phosphoric acid is agitated with an equal volume of

water, the latter removes practically all the acid just as in the case of sulphuric and hydrochloric acids.

When a very highly concentrated liquid phosphoric acid is agitated with ether, the two mix completely with large development of heat, and ether may be added in any proportion without causing any precipitation. If a small quantity of water is added, it mixes completely, but if the addition of water is continued, there at last comes a point when a small quantity of ether separates, highly charged with phosphoric acid. The addition of more water causes the separation of a larger volume of ether containing a lower proportion of acid, and still more water separates a still larger volume of ether containing still less acid, and this change continues as the addition of water is continued, until the coefficient already stated is reached. These highly concentrated liquids cannot, however, be regarded as simple aqueous solutions of phosphoric acid; they are really complex liquids containing water, phosphoric acid, and a compound of phosphoric acid and ether. Quantitative details of the experiments are given. C. H. B.

**Degree of Dissociation of Electrolytes at 0°.** By MEJER WILDERMANN (*Phil. Mag.*, 1896 [5], 42, 102—103).—The author points out that Wood has wrongly attributed certain molecular freezing point depressions to him, and that, contrary to Wood's statement, in the paper cited Arrhenius's generalisation finds an excellent confirmation. H. C.

**Influence of the Temperature of the Cold Jacket on Cryoscopic Measurements.** By FRANÇOIS M. RAOULT. (*Zeits. physikal. Chem.*, 1896, 20, 601—604.)—The observed freezing point is that temperature at which the velocity of cooling by radiation is equal to the velocity of heating by ice-formation. The latter velocity is proportional to the difference between the observed and true freezing point, that is, $t_0 - t_1$, hence also the velocity of cooling is so proportional, namely, $v = k(t_0 - t_1)$ or $(t_0 - t_1) = v/k$, a result similar to that of Nernst and Abegg. (Abstr., 1895, ii, 155). The true freezing point can, however, be readily found by observing the apparent freezing point at two or three different temperatures of the cold jacket, other conditions being similar. The values of $v$ (the velocity of cooling) are taken for abscissæ and the observed freezing points, $t_1$, as ordinates and the curve (a straight line) produced to the value $v = 0$. The author finds that with solutions of the same substance at various concentrations, the difference $t_0 - t_1$ is proportional to the concentration, consequently to the depression, hence if $C_0$ and $C_1$ are the true and apparent depressions $t_0 - t_1 = qC_0$ and $C_1 - C_0 = t_0 - t_1$ hence $C_1 = C_0(1 + q)$ so that laws deduced for $C_0$ hold also for $C_1$ since $q$ is a constant dependent only on the nature of the dissolved substance. In the author's experiments, $q$ had the following values: pure water, −0·001; sulphuric acid, 0·004; hydrogen chloride, 0·002; cane sugar. 0·002; alcohol, 0·005. It follows therefore that the temperature of the bath does not invalidate laws deduced from the freezing point depressions of various solutions of the same compound and also that the effect is very slight and does not noticeably affect the actual values of molecular depressions of different compounds, or the deduced laws, and further the effect can be readily allowed for and corrected. L. M. J.

NOTE BY ABSTRACTOR.—The above expression is deduced in a manner closely analogous to that employed by Wildermann (Abstr., 1896, ii, 291) with which it entirely agrees if the value $k(ts - t_1)$ is substituted for $v(ts =$ convergence temperature).

**Parabromotoluene as a Solvent in Cryoscopic Researches.**—By EMANUELE PATERNÒ (*Gazzetta*, 1896, **26**, ii., 1—9).—The author has studied the possibility of using parabromotoluene as a solvent in cryoscopic determinations; the molecular depressions of the freezing point of parabromotoluene melting at 26·88° by benzene, toluene, ethylenic bromide, ethylsuccinimide, ethylic oxalate, veratrole, thiophen, aniline, pyridine, ethylic alcohol, acetic acid, phenol, paracresol, and thymol were determined, and from the results it is concluded that the value 82·20 calculated by van't Hoff's formula from the latent heat of fusion is the normal value of this constant.

Parabromotoluene behaves in cryoscopy similarly to the hydrocarbons and their halogen and nitro-derivatives, giving normal results with neutral substances and bases, but only about half the normal molecular depressions with acids; with alcohols and phenols, the molecular depressions are practically normal in very dilute solutions, but, as the concentration is increased, the molecular depressions decrease rapidly with alcohols, and less rapidly with phenols.

Since parabromotoluene is easily purified, little liable to change, and does not exhibit superfusion, it should constitute a valuable solvent in cryoscopy. W. J. P.

**Veratrole as a Solvent in Cryoscopic Researches.**—By EMANUELE PATERNÒ. (*Gazzetta*, 1896, **26**, ii, 9—16).—Cryoscopic determinations of benzene, paraxylene, bromotoluene, thiophen, aniline, pyridine, ethylic alcohol, glycerol diethylic ether, benzylic alcohol, phenol, thymol, acetic acid, and valeric acid in veratrole solution give 64 as the mean molecular depression of the freezing point of this solvent. Veratrole is not cryoscopically analogous in behaviour to the hydrocarbons or their halogen or nitro-derivatives but gives almost the same molecular depressions of the freezing point with substances of very varied types; with aniline, phenol and thymol the molecular depressions are extraordinarily constant with change of concentration. The cryoscopic behaviour of veratrole is in many respects similar to that of benzophenone. W. J. P.

**Nitrobenzene as a Solvent in Cryoscopic Research.**—By G. AMPOLA and E. CARLINFANTI (*Gazzetta*, 1896, **26**, ii, 76—91).—From determinations of the depression of the freezing point of nitrobenzene by benzene, bromobenzene, toluene, bromotoluene, paraxylene, benzaldehyde, veratrole, naphthalene, ethylic oxalate, thiophen, chloroform, bromoform, formic acid, acetic acid, valeric acid, isobutyric acid, ethylic alcohol, isopropylic alcohol, isobutylic alcohol, caprylic alcohol, trimethylcarbinol, benzylic alcohol, cinnamic acid, glycerol ethylic ether, phenol, thymol, paracresol, aniline, dimethylaniline, coniine, quinoline, pyridine, and piperidine, the authors find the molecular depression to be 69, the number calculated by van't Hoff's formula being

68·6. The determinations indicate that the behaviour of nitrobenzene as a solvent is analogous to that of benzene, bromoform, paraxylene and parabromotoluene. Paraxylene, benzene, toluene, veratrole, naphthalene, bromoform, chloroform, bromobenzene, bromotoluene, ethylic bromide and benzaldehyde give normal depressions, as does also thiophen, although it behaves abnormally in benzene solution. Aniline and dimethylaniline give very constant molecular depressions between very wide limits of concentration; quinoline is also nearly normal in behaviour, and the irregularities noted with the other bases examined is certainly due to reaction occurring between the dissolved substance and the solvent. The behaviour of acids, alcohols and phenols is strictly analogous to their behaviour in benzene, paraxylene and bromoform. W. J. P.

**Behaviour of Phenol as a Solvent in Cryoscopy.** By EMANUELE PATERNÒ (*Gazzetta*, 1896, **26**, ii, 363—374).—The author has made series of determinations of the molecular depression of the freezing point of phenol by water, bromoform, toluene, paraxylene, nitrobenzene, parabromotoluene, veratrole, ethylic oxalate, alcohol, benzylic alcohol, glycerol diethylic ether, thymol, methylic salicylate, formic acid, acetic acid, valeric acid, pyridine, aniline, dimethylaniline, and ethylsuccinimide. The molecular depressions of the freezing point by bromoform, nitrobenzene, toluene, parabromotoluene, and paraxylene diminish gradually as the concentration increases; this behaviour is different from that observed with other hydrocarbons and their halogen derivatives by Eijkman (Abstr., 1890, 324) who found that the molecular depressions tended to increase with the concentration. The alcohols and phenols behave very regularly and the molecular depressions are very constant between wide limits of concentration; with the diethylic ether of glycerol, which is a secondary alcohol, the molecular depression is not nearly so constant. The tendency of the molecular depression to increase with the concentration, noticed by Eijkman with phenolic substances in phenol solution, is not confirmed by the author; the molecular depressions caused by thymol and methylic salicylate gradually decrease as the concentration increases, and Garelli and Montanari have observed similar behaviour in the case of the dihydroxybenzenes. The molecular depression caused by acids is small, even in dilute solutions, and it decreases considerably as the concentration increases: this result agrees with that obtained by Eijkman. The rate of increase of the molecular depression with concentration caused by pyridine, aniline, and dimethylaniline is not so great as in the case of the alkaloids studied by Eijkman; the molecular depression for ethylsuccinimide, however, increases rapidly with the concentration. Veratrole and ethylic oxalate give high molecular depressions which also increase with the concentration. Water in dilute solutions gives a low molecular depression which rapidly increases with the concentration; this substance behaves, therefore, similarly to the acids.

Phenol seems to differ in behaviour from other solvents used in cryoscopic work, in that there is a general tendency for the molecular

depressions to increase with the concentration, whilst in general the molecular depression decreases as the concentration increases

W. J. P.

**The Cryoscopic Behaviour of Substances similar in Composition to the Solvent.** By FELICE GARELLI (*Gazetta*, 1896, 26, ii, 380–387).—Cryoscopic determinations show that cyclopentadiene (Abstr., 1896, i, 289), as would be expected from the author's previous results (*ibid*, ii, 292), forms solid solutions with freezing benzene but behaves quite normally in paraxylene solution. Dicyclopentadiene, however, behaves quite normally in freezing benzene, phenanthrene naphthalene, and diphenyl.

Fluorene gives normal results in benzene and naphthalene solution, but the addition of fluorene to phenanthrene raises the freezing point of the latter, owing to the formation of a solid solution. W. J. P.

**Osmotic pressure of Ether and Chloroform in the Nerve Cells.** By HEINRICH DRESER. (*Zeits. physikal. Chem.*, 1896, 21, 108—112)—The best narcotising mixture in the case of chloroform is 10 grams in 100 litres of air, in the case of ether 20 grams in the same volume. Assuming that the protoplasmic solution is in equilibrium with this mixture, the author calculates the osmotic pressure of the two compounds in their solution, the results being 982·4 atmospheres and 703·6 atmospheres for the chloroform and ether respectively. L. M. J.

**Labile Equilibrium of Salt Solutions.** By ADOLF BLÜMCKE (*Zeits. physikal. Chem.*, 1896, 20, 586—592).—Contains thermodynamical diagrams representing states of labile equilibrium of salt solutions. (Abstr. 1893, ii, 447). L. M. J.

**Hypothesis of the Coloration of Ions.** By GAETANO MAGNANINI (*Gazzetta*, 1896, 26, ii, 92—96. Compare Magnanini and Bentivoglio, Abstr., 1894, ii, 129).—Determinations of the electrical conductivity of dimethylvioluric acid give $K = 0·00157$ and $\mu \propto = 352$; the potassium salt is much more highly dissociated in solution and $V = 1280$, $\mu = 96·3$. Solutions of the acid, in accordance with Ostwald's hypothesis of the coloration of the ions, are less strongly coloured than those of the salt.

With solutions of isonitrosodiketohydrindene, the values $K = 0·0000105$ and $\mu \propto = 355$ were obtained; the yellow colour of the solid substance persists in solution, but highly dilute solutions are of a more reddish tint.

Diethylic dichloroquinonedimalonate (Grindley and Jackson, Abstr., 1893, i, 312) is yellow in the solid state, and nearly insoluble in water; when heated with water, a small quantity dissolves, and the solution becomes blue, whilst on cooling the substance crystallises out, the solution becoming colourless and having a much smaller electrical conductivity when cold than when hot. On adding a trace of acid, the salt dissolves and the solution becomes deep blue. W. J. P.

**Transparency of Solutions of Colourless Salts.** By WALTHÈRE

SPRING (*Zeits. anorg. Chem.*, 1896, **13**, 19—28).—Solutions of various strengths of the following carefully purified salts were examined: lithium chloride, sodium chloride and nitrate, potassium bromide, chloride and nitrate, and the chlorides of magnesium, calcium, strontium, and barium. The relative amount of light absorbed by a column of each salt solution is determined by comparing it with an equal column of water, using glass plates to equalise the transparency of the two columns. The relative absorption of the salt solutions compared with water is then calculated from the equation $J_2 = J_1 C^{a(n_1-n_2)}$ when $a$ = the absorption of one glass plate, $n$ = the number of plates used, and $J_1$ = the intensity of the light after passing through the water.

The results obtained show that the colour of a column of water is not altered by the presence of dissolved salts, and all the salt solutions gave the same spectrum as pure water. The transparency of the solution depends on the nature of the dissolved salt and on the concentration: it increases as the concentration decreases, but is not proportional to the concentration. The absorption of a salt solution does not equal the sum of the absorptions of the solvent and the dissolved salt. E. C. R.

**Autocatalysis.** By F. G. DONNAN (*Ber.*, 1896, **29**, 2422—2423).—The equation $dx/dt = km\ (a - x)^2$, which Goldschmidt has shown (Abstr., 1896, ii, 638) to express the velocity of etherification in alcoholic solution, is identical, since $m$ is constant, with the equation $dx/dt = km^2\ (a - x)^2$ which should express the velocity of etherification if no autocatalysis occurs: if the hydrogen ions acted catalytically according to a linear law, the equation $dx/dt = k_1\ m^3\ (a - x)^3$ should hold. The author therefore concludes that no autocatalysis occurs during direct etherification. The fact that etherification is a bimolecular reaction, as Goldschmidt finds, is a necessary consequence of the electrolytic dissociation and is in itself proof of the non-occurrence of autocatalysis; etherification is a similar reaction to the formation of carbamide from ammonium cyanate (Walker and Hambly, *Trans.*, 1895, 746). W. J. P.

**Velocity of Decomposition of some Sulphur and Phosphorus Compounds by Water.** By GIACOMO CARRARA and I. ZOPPELARI (*Gazzetta*, 1896, **26**, i, 483—493). In continuation of their previous work (Abstr., 1894, ii, 412), the authors have determined the velocity of reaction in non-homogeneous systems consisting of water and the compounds named in the appended table, using for calculation the formula

$$\frac{1}{t\,O}\log\frac{A}{A-x} = AC,$$

in which $O$ is the surface area of the two liquids in contact, $A$ the quantity of decomposable liquid, $x$ the quantity of the latter decomposed during the time $t$, and $C$ is a constant. The sp. gr. $d$ of the liquids at 11°/4°, and the temperature $T$ at which the experiments were made are also given; both $AC$ and $x/t$ are calculated.

The quantity $AC$ deduced from the logarithmic formula is in all

cases more constant than the ratio $x/t$, thus confirming the authors view that the logarithmic expression should be used in non-homogeneous systems.

| Substance | $d$ | $T$ | $A$ | $AC$ | $\frac{x}{t}$ |
|---|---|---|---|---|---|
| $SOCl_2$ | 1·6577 | 1° | 1 | 0·0152 | 0·0317 |
| $S_2O_5Cl_2$ | 1·8512 | 10 | 1 | 0·00331 | 0·00571 |
| ,, | ,, | 30 | 1 | 0·0100 | 0·0160 |
| $PCl_3$ | 1·5941 | 5 | 1 | 0·000297 | 0·0071 |
| $PBr_3$ | 2·9132 | 5 | 10 | 0·0111 | 0·0239 |
| ,, | ,, | 10 | 10 | 0·0212 | 0·0442 |
| $POCl_3$ | 1·6529 | 5 | 10 | 0·000348 | 0·0782 |
| ,, | ,, | 10 | 10 | 0·00067 | 0·0138 |
| $PSCl_3$ | 1·6531 | 10 | 10 | 0·000132 | 0·000289 |
| ,, | ,, | 30 | 10 | 0·000238 | 0·00041 |

W. J. P.

**Velocity of Formation of Alkali Xanthogenates [Alkali Ethylic $\alpha\beta$-dithiocarbonates].** By NATALE VIANELLO MORO. (*Gazzetta*, 1896, **26**, i, 494—501).—If a satisfactory inactive solvent could be found, the formation of an alkali xanthogenate [ethylic $\alpha\beta$-dithiocarbonate] in accordance with the equation $CS_2 + KHO + EtOH = CS_2OEtK + H_2O$, would constitute a reaction of the third order, and might then be advantageously studied, because the velocities of very few such reactions have been determined. Since such a solvent could not be found, the reaction was examined in alcoholic solution, and, as was to be expected, then proceeded as a reaction of the second order, the quantity of alcohol present being a constant. W. J. P.

**Hydrolysis of Ferric Chloride.** By H. M. GOODWIN (*Zeits. physikal. Chem.*, 1896, **21**, 1—15).—When a neutral solution of ferric chloride is considerably diluted, the solution, although colourless at first, soon becomes yellow, whilst also the molecular conductivity increases with the time since dilution. The author finds the velocity of the change of conductivity increases with the dilution, and that the change does not commence until some time after dilution, this time increasing with the concentration. The time required to reach a final state of equilibrium is also very variable, being 3 hours for 0·0001 N, and a week for 0·0006 N. The velocity of the change, when once started, rapidly increases, reaches a maximum, and then decreases. The author considers that these anomalies are due to the hydrolysis of the ferric chloride on dilution, in accordance with the equation $FeCl_3 + H_2O = FeOH'' + H' + 3Cl'$, in which case an increase in conductivity is caused by the greater velocity of the new ions. The slow after increase is caused by the further hydrolysis and formation of the colloïdal hydroxide. Conductivity and cryoscopic measurements yield numbers which are in accord with this view, but not with the view that hydrolysis to $Fe(OH)_3$ occurs immediately after dilution.

L. M. J.

**Velocity of the reaction between Ferric Chloride and Stannous Chloride.** By ARTHUR A. NOYES (*Zeits. physikal. Chem.*, 1896, 21, 16.)—The author's opinion that the reaction between ferric chloride and stannous chloride is one of the third order is contrary to that of Kortright, who considered that, if hydrolysis of the ferric chloride to ferric hydroxide is allowed for, the reaction is of the second order (Abstr., 1895, ii, 159 and 257). The results obtained by Goodwin (preceding abstract) show that hydrolysis to ferric hydroxide can occur only to a very small extent, so that Kortright's explanation cannot hold.
L. M. J.

**Explosions.** By C. HOITSEMA (*Zeits. physikal. Chem.*, 1896, 21, 137—148).—The first explosive decomposition studied was that of silver oxalate, $Ag_2C_2O_4 = Ag_2 + 2CO_2 (= 29500$ Cal.). Preliminary experiments proved that the same products were obtained during slow decomposition. The velocity constant was found to increase with the temperature, the curve bending upwards very rapidly at about 165°. When the reaction velocity was then carefully determined at fixed temperatures, satisfactory constancy was found, the mean results for 150°, 155°, 160° and 170° being respectively 0·00292, 0·00481, 0·00711 and 0·0174, values which satisfactorily obey Nernst's expression $\log k = -A/T + c$. Sulphide of nitrogen was qualitatively examined, and was found to give the same products whether the decomposition was slow or rapid. The velocity was found further to increase with the temperature. Mercury and silver fulminates were also examined, but in this case the products of decomposition depend on the velocity of decomposition and no quantitative measurements were made.
L. M. J.

**The Theory of "Corresponding" States.** By G. BAKKER (*Zeits. physikal. Chem.*, 1896, 21, 127—133).—The author deduces the following conclusions respecting compounds obeying Van der Waals' laws, at "corresponding" states. (1) The deviations from the laws of Joule, Boyle, and Gay Lussac are equal. (2) The change in the molecular entropy by vaporisation is equal for all compounds. (3) The molecular entropy is equal. (4) The specific heat is inversely proportional to the molecular weight. (5) The molecular energy and the molecular free energy are proportional to the critical temperature. (6) The velocity of sound is directly proportional to the critical temperature and inversely proportional to the molecular weight.
L. M. J.

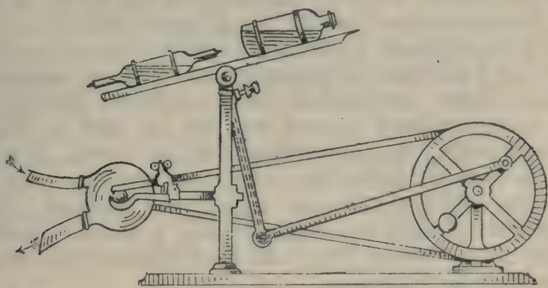
**Isomorphism XII.** By JAN W. RETGERS (*Zeits. physikal. Chem.* 1896, 20, 481—546).—Beryllium is frequently regarded as isomorphous with the elements of the zinc group, chiefly owing to the form resemblance of some of its mineral compounds to those of zinc, and tothe alleged isomorphous mixtures of beryllium sulphate with the vitriols (Klatzo, *J. pr. Chem.*, 1869, 106, 227). The minerals helvite and danalite, in which mixtures of silicates and sulphides of beryllium manganese, iron and zinc are found, are composed of the silicate of the former combined with the isomorphous mixture of the other

silicate and the sulphides, that is, $3Be_2SiO_4,3(MnFe)SiO_4,2(MnFe)S$ represents helvite. Similar remarks apply to other beryllium minerals which are shown to contain no isomorphous mixtures of beryllium silicate with the silicates of the zinc group. The author endeavoured to prepare mixed crystals of beryllium sulphate with the sulphates of copper, nickel, iron and manganese, but although several solutions were in each case crystallised no trace of mixed crystals was obtained, a result completely at variance with the results of Klatzo, but agreeing with those of Marignac. From this, the author concludes that beryllium salts are not isomorphous with the salts of the metals of the magnesium group. The author adds other examples of the use of etched-figures (Abstr., 1895, ii, 309) in the determination of isomorphism. In all the cases hitherto examined, isomorphous compounds show similar etched-figures when subjected to the same reagent, but the converse does not necessarily hold, so that although rutile, zircon, and tinstone give similar figures with hydrogen potassium fluoride, the author does not consider them isomorphous, while the isomorphism also of silicon and titanium compounds is doubtful. This method is also useful in examining cases of hemimorphism, and cases are recorded where supposed hemihedral compounds are proved to be holohedral, as, for instance, copper oxide, and phosgenite [cromfordite].

Cases of anomalous mixtures are next considered. Many salts in crystallising absorb organic colouring matters, and frequently such mixtures have a more or less fibrous structure; probably the origin of many fibrous minerals is due to a similar cause. The colour also of various minerals may be due to organic mixtures, as, for example, yellow blende (free from iron), topaz, amethyst, rose quartz, &c. Some minerals also form anomalous mixtures with others, thus the oxides of tin and titanium form crystals coloured by ferric, chromic or manganic oxides. The cause of this is not clear but it may be due to a crystallographic opposition, the axes of one being parallel to the interaxes of the second. Numerous examples of other anomalous mixtures are recorded. L. M. J.

**Isomorphism of Alkali Salts.** By R. KRICKMEYER (*Zeits. physikal. Chem.*, 1896, 21, 53—89). The specific gravity of isomorphous mixtures is stated by Retgers to be a purely additive function, and the experiments of the author on the specific gravities of isomorphous mixtures of potassium and ammonium salts verify this conclusion, hence the sp. gr. of crystals is used as a test for mixtures. Such mixtures were obtained in the case of the potassium and ammonium alums, the monoclinic double sulphates with zinc, nickel, &c., and the chlorides. With the phosphates and tartrates, however, the miscibility of the salts was very slight. In the case of sodium and potassium salts no mixed crystals could be obtained although the alums, double sulphates with zinc, &c., chlorides, and bromides were investigated. Sodium and ammonium chlorides, lithium and sodium chlorides and sulphates, lithium and potassium chlorides and sulphates, were also examined but in no case could mixed crystals be obtained, so that the only truly isomorphous compounds are those of potassium and ammonium. The paper contains a number of carefully determined specific gravities of the salts examined. L. M. J.

**A New Shaking Apparatus for the Laboratory.** By Max von Recklinghausen (*Ber.*, 1896, 29, 2372—2373).—The apparatus is represented in the diagram one-tenth its natural size. Its advantages



are (1) That friction is reduced to a minimum. (2) That the different parts are not corroded by the air of the laboratory. (3) That only a small force is needed to set the apparatus in motion. The platform consists of an iron frame covered with coarse wire gauze, to which the flasks, &c., to be shaken can easily be strapped. J. J. S.

---

## Inorganic Chemistry.

**Does Hydrogen find its Proper Place at the Head of Group I. or at the Head of Group VII. ?** By Orme Masson (*Chem. News*, 1896, 72, 283—284).—As reasons for assigning a position to hydrogen at the head of Group VII. in the periodic system, the author points to its monad valency, its diatomic molecule, its gaseous character and extremely low boiling-point. The atomic weight of hydrogen places it rather in Group VII. than in Group I., and arguments based on substitution cut both ways, as an inorganic chemist would be most struck with the analogy between hydrogen and the alkali metals, an organic chemist with the analogy between hydrogen and the members of the chlorine group.

John A. R. Newlands (*ibid.*, 1896, 72, 305) points out that in 1872 he classed hydrogen and chlorine together on account of their mutual replaceability, and because the atomic weight of hydrogen indicates that it is really the lowest member of the chlorine group.

H. C.

**Slow Oxidation of Hydrogen and of Carbonic Oxide.** By Victor Meyer and Max von Recklinghausen (*Ber.*, 1896, 29, 2549 – 2560).—It is known that hydrogen is slowly oxidised, when led through a solution of potassium permanganate, and a repetition of this experiment showed that the gas if left over an alkaline or neutral solution of the salt slowly decreased in volume until all had been absorbed. Carbonic oxide behaved similarly.

On shaking the mixture on the shaking-machine lately devised by von Recklinghausen, a similar result was arrived at; if, however, an acid solution of permanganate was employed, a large volume of gas remained unabsorbed, which on examination was found to be oxygen. 39 c.c. of hydrogen after shaking for 15 hours with 29 c.c. of an acid solution of permanganate yielded 17·8 and 20·4 c.c. of oxygen.

Since an acid solution of permanganate evolves oxygen by itself on standing, three experiments were conducted side by side, the hydrogen being replaced in one case by air and in the other by carbonic anhydride; the quantities obtained were, however, very different, the carbonic anhydride experiment yielding only 2·5 c.c. of oxygen, whilst with the hydrogen 19·1 c.c. was obtained. The amount of oxygen evolved does not increase after a certain limit has been reached, the same volume being obtained whether the mixtures were shaken for 17 or for 87 hours.

The quantity of oxygen evolved from an acid solution of permanganate on standing differs considerably from that given off on shaking. A closed tube completely filled with the solution burst after standing $2\frac{1}{2}$ months in the dark, whilst one which had been filled one-third with permanganate and two-thirds with air was found to contain 50 c.c. of oxygen at the end of the same period, that is, nearly 20 times as much as was given off in the majority of the experiments when the liquid was shaken. It was further found that the temperature had a considerable influence on the amounts evolved.

The formation of oxygen in these experiments could be readily understood on the supposition that hydrogen peroxide was at first produced and that this subsequently reacted with the permanganate, evolving oxygen. Since, however, carbonic oxide behaves in a precisely similar way (yielding 14·5—11·5 c.c. of oxygen when 39·5 c.c. of the gas is shaken with 20 c.c. of permanganate solution for $23\frac{1}{2}$ hours), this explanation does not hold good.

The evolution of oxygen is irregular, and the numbers obtained are merely approximate, the quantities evolved in two similar experiments seldom agreeing.

It might be supposed that the large quantity of oxygen evolved might be due to the diminution of pressure consequent on the absorption of the hydrogen; that this is not the case, however, was shown by shaking carbonic anhydride and air with permanganate under diminished pressure, the volume of oxygen given off (2—3 c.c.) remaining unaltered.

The authors hope to throw light on these phenomena by means of further experiments conducted on other reducing gases, such as the hydrocarbons, &c. Meanwhile, they consider that the most probable explanation is that put forward by van't Hoff in explanation of the simultaneous oxidation of triethylphosphine and indigo solution, namely, that in slow oxidations the oxygen molecule acts as two atoms (?) or ions (?). The reaction in this case proceeding thus

$$\begin{matrix} H_2 \\ H_2 \end{matrix} + \begin{matrix} OO \\ OO \end{matrix} = 2H_2O + O_2$$

the quantity of oxygen given off agreeing approximately with this equation. J. F. T.

**Behaviour of Halogen Hydrides at Low Temperatures.** By THADDAEUS ESTREICHER (*Zeits. physikal. Chem.*, 1896, **20**, 605—609).—The author has determined the boiling points and freezing points of hydrogen chloride, bromide, and iodide, as well as the critical temperatures of the last two compounds. The low temperatures were obtained by means of ethylene, and by carbonic anhydride and ether, and were measured by a helium thermometer. (Abstr., 1896, ii, 597). The results obtained were

| | Pressure | b. p. | m. p. | Crit. temp. |
|---|---|---|---|---|
| Hydrogen chloride ... | 745·2 | −83·7° | −111·1° | — |
| Hydrogen bromide .. | 738·2 | −64·9° | − 87·9° | + 91·3° |
| Hydrogen iodide...... | 739·8 | −34·1° | − 50·8° | +150·7° |

The liquid was in each case clear and colourless, and the solid an iron grey mass, but in the case of the iodine compounds the products were frequently coloured by dissolved iodine. L. M. J.

**Crystallography of Iodates and Periodates.** By ARTHUR S. EAKLE (*Zeit. Kryst. Min.*, 1896, **26**, 558—588).—The author has investigated the conditions of growth most favourable to the cultivation of well-developed crystals of a number of salts and determined their geometrical and optical properties.

Well-developed transparent hydrated crystals of the trigonal pyramidal sodium periodate, $NaIO_4 + 3H_2O$, can be obtained by very slow spontaneous evaporation of the pure aqueous solution, but in a much shorter time from solutions containing sodium nitrate; $a : c = 1 : 1·0942$. The crystals deposited from a pure aqueous solution consist of dextrogyrate and lævogyrate individuals in approximately equal numbers, but in solutions containing sodium nitrate the remarkable fact is observed that the lævogyrate crystals outnumber the dextrogyrate ones by about four to one. The anhydrous ditetragonal dipyramidal crystals of sodium periodate, $NaIO_4$, deposited from aqueous solution at above 30° have the axial ratio $a : c = 1 : 1·5900$.

Aqueous solutions of ammonium periodate containing ammonia deposit, on spontaneous evaporation, trigonal rhombohedral crystals having the composition $(NH_4)_4I_2O_9,3H_2O$, and the axial ratio $a : c = 1 : 1·6118$; when the solution during evaporation has lost nearly all its free ammonia, crystals of the normal periodate, $NH_4IO_4$, isomorphous with those of anhydrous sodium periodate, separate; $a : c = 1 : 1·5228$. Aluminium periodate, $Al(IO_4)_3 + 3H_2O$, crystallises in holohedral cubic forms from a solution containing nitric acid.

Rhombic bipyramidal crystals of anhydrous sodium iodate, $NaIO_3$, are deposited from an aqueous solution at 100°; $a : b : c = 0·9046 : 1 : 1·2815$; at lower temperatures, long needles of the hydrated salt are

deposited. Ammonium iodate, $NH_4IO_3$, crystallises in long prisms; $a : b : c = 0·9948 : 1 : 1·4335$. Silver iodate, $AgIO_3$, in thin, colourless, transparent plates of adamantine lustre from solutions containing ammonia; $a : b : c = 0·8832 : 1 : 1·3072$. These three salts are isomorphous.

Potassium iodate is cubic and holohedral, but the habit of the crystals varies widely with changes in the temperature of crystallisation; the crystals are isomorphous with those of rubidium iodate, which consist of opaque, white cubes.

Calcium iodate, $Ca(IO_3)_2 + 6H_2O$, separates from an aqueous or nitric acid solution in rhombic prisms; $a : b : c = 0·4357 : 1 : 0·5231$. If, however, the solution contains a small quantity of calcium chromate, a second form of calcium iodate having the same composition, is deposited; the new crystals are rhombic pyramidal prisms; $a : b : c = 0·64652 : 1 : 0·27682$. Calcium iodate is thus dimorphous.

The double compound of sodium iodate and iodide, $2NaIO_3$, $3NaI_1 + 20H_2O$, crystallises in dihexgonal bipyramidal prisms; $a : c = 1 : 2·1892$. Rubidium nitrate crystallises in ditrigonal scalenohedral prisms; $a : c = 1 : 1·2360$.

The crystallographic properties of the rhombic aluminium nitrate, $Al(NO_3)_3 + 9H_2O$, the monoclinic barium chlorate, $Ba(ClO_3)_2 + H_2O$, and the rhombic barium permanganate, $BaMn_2O_8$, were also determined.

W. J. P.

**Reduction of Sulphuric Acid by Copper, as a Function of the Temperature.** By Launcelot W. Andrews (*J. Amer. Chem. Soc.*, 1896, **18**, 251—254).—By means of suitable apparatus, the author has been able to show—(1) That sulphuric acid (98·4 per cent.) begins to appreciably dissociate at a temperature somewhat below 70°, probably 67°; (2) That sulphuric acid in the presence of air or oxygen will dissolve copper at the ordinary temperature, without the evolution of a trace of sulphurous anhydride; (3) That the reduction of sulphuric acid by copper does not begin below 86°, that is, not until the acid has become partly dissociated into anhydride and water. Baskerville's statement (Abstr., 1896, ii, 474) that sulphuric acid is reduced by copper at 0° is therefore incorrect.

J. J. S.

**Free Hydrazine.** By Cornelis A. Lobry de Bruyn (*Rec. Trav. Chim.*, 1896, **15**, 174—184; Compare Abstr., 1895, ii, 347).—Free hydrazine is best prepared by the action of barium oxide on hydrazine hydrate. The hydrate is added in small quantities at a time to the barium oxide contained in a flask, which is cooled from time to time and should be provided with a neck some 50 cm. long, bent at right angles at its upper end so that it can be directly attached to the condenser. The flask is first heated for several hours in a glycerol bath at 110—120°, and the contents are then distilled under a pressure of 150—100 mm. To prevent oxidation, the apparatus is filled with dry hydrogen. The base, which is collected in a cooled receiver, still contains 3—4 per cent. of water, and is, therefore, again distilled in a smaller flask, with a little barium oxide, the apparatus again being filled with dry hydrogen.

The free base melts at 1·4°; it can, however, be cooled several degrees below this before it freezes. Its boiling points, determined in an atmosphere of dry hydrogen, are 56° at 71 mm., 113·5° at 761·5 mm., and 134·6° at 1490 mm. pressure. Its sp. gr. = 1·014 at 15°/15°, that is, almost the same as that of the hydrate.

The refractive index, as determined by Eijkman, is given as

| | nβ | nα | A | β – α |
|---|---|---|---|---|
| | 1·47988 | 1·46953 | 1·45693 | 0·01035 |
| Gladstone's formula.. | 15·18 | 14·86 | 14·46 | 0·33 |
| Lorentz's formula ... | 8·99 | 8·82 | 8·62 | 0·17 |

d = 1·0114 t = 17·8° MV = 31·64.

Calculated for the group $NH_2$, the dispersion = 0·16 according to Gladstone's formula and 0·09 according to Lorentz. These numbers are practically the same as those calculated from pentamethylenediamine (*Rec. Trav. Chim.*, 1893, **12**, 281).

As regards its solubility, hydrazine resembles both water and hydroxylamine; it is miscible in all proportions with methylic, ethylic, propylic, isobutylic, and amylic alcohols, but is only very sparingly soluble in other organic solvents. Many salts dissolve in it, and determinations of their solubilities are given.

Hydrazine apparently combines with sodium chloride, as a considerable amount of heat is developed on mixing the two and the whole sets to a crystalline mass on cooling. Ammonium salts are decomposed by the base, and lead nitrate is dissolved by it. The base itself may be heated to 300—350° without undergoing perceptible decomposition; even after heating for an hour at the boiling point of sulphur part of it remains unaltered.

The critical temperature, as determined in Altschul's apparatus (*Zeits. physikal. Chem.*, 1893, **11**, 582) is 380°. According to Boltwood, stability of the base at high temperatures depends on the pressure. The decomposition first proceeds according to the equation

$$2N_2H_4 = N_2 + H_2 + 2NH_3,$$

but the final decomposition is $3N_2H_4 = N_2 + 4NH_3$.

The base is a strong reducing agent, it readily bursts into flame in chlorine; bromine and iodine also react violently. It is slowly oxidised by dry air free from carbonic anhydride, and also by oxygen; in the latter case, the temperature gradually rises to 100°, and ammonia can readily be recognised. Yellow phosphorus also acts on an aqueous solution of the base, forming, probably, hydrides of phosphorus.

Sodium reacts with the base suspended in dry light petroleum, yielding hydrogen, ammonia, and a brown solid substance.

J. J. S.

**Oxidation by means of Hydroxylamine.** By Fritz Haber (*Ber.*, 1896, **29**, 2444—2445).—Hydroxylamine readily converts

ferrous hydroxide into the ferric compound, and may be recognised by this reaction, which is not given by hydrazine. The hydroxylamine is almost completely converted into ammonia.

An interesting lecture experiment to illustrate the double function of hydroxylamine as an oxidising and reducing agent may be carried out by adding hydroxylamine hydrochloride to a hot emulsion of ferrous hydroxide precipitated by means of caustic soda. The greenish mass rapidly becomes reddish brown, owing to the oxidation of the hydroxide. If now the liquid be acidified and a fresh quantity of hydroxylamine hydrochloride added, the latter acts as a reducing agent, and rapidly converts the ferric into a ferrous salt, the change being rendered evident by the disappearance of the yellow colour.

A. H.

**Nitrohydroxylamine.** By ANGELO ANGELI (*Gazzetta*, 1896, **26**, ii, 17—25).—On treating hydroxylamine with acidic chlorides or anhydrides, or with an alkylic salt of an organic acid in alkaline solution, derivatives having the constitution R·CO·NH·OH or OH·CR:N·OH are obtained. It seemed of interest to endeavour to prepare a substituted hydroxylamine, in which the acidic group was an inorganic acidic radicle. With this object, a cold saturated solution of hydroxylamine hydrochloride (1 mol.) is poured into a concentrated alcoholic solution of sodium ethoxide (3 mols.), and to this, after filtration, ethylic nitrate (1 mol.) is added; a white precipitate of *sodionitrohydroxylamine*, $Na_2N_2O_3$, separates immediately, but cannot be further purified because of its great solubility in water. On adding barium chloride to its dilute aqueous solution, a heavy, white, minutely crystalline precipitate of the corresponding *barium* salt, $BaN_2O_3 + H_2O$, is deposited; it loses its water at 115—120°.

On treating either the sodium or barium salt with a mineral acid, a violent evolution of nitric oxide occurs, almost quantitatively in accordance with the equation, $H_2N_2O_3 = H_2O + 2NO$; the salts also decompose on heating, giving nitric oxide, and leaving the metallic oxide. The aqueous solution of the sodium salt is readily decomposed by boiling, and nitrites and nitrates formed from the nitric oxide evolved are found in solution; the barium salt is not decomposed by prolonged boiling with water, and is much more stable in the air than the sodium salt.

The aqueous solution of the sodium salt gives a white precipitate with lead acetate or cadmium sulphate; a yellow solution, which rapidly deposits mercury, with mercuric chloride; a deep brown-red coloration, which disappears on boiling, with uranium nitrate; and a yellow precipitate, which rapidly blackens, with silver nitrate; it reduces Fehling's solution, and gives a violet to brown coloration with ferric chloride.

Mixtures of the sodium salt with sodium thiocyanate or hypophosphite, or with antimony trisulphide and sulphur or carbon, explode violently when struck; when mixed with red phosphorus, the sodium salt also detonates if struck, but the mixture is less sensible to shock than that of red phosphorus with potassium chlorate.

According to its method of formation, nitrohydroxylamine should have the constitution $NO_2 \cdot NH \cdot OH$; it might readily undergo intramolecular change and assume the constitution $OH \cdot N \colon NO \cdot OH$ or $\begin{matrix} HO \cdot N \\ HO \cdot N \end{matrix} > O$.

It is interesting to note that nitrohydroxylamine is the last missing member of the series of acids corresponding with the five oxides of nitrogen; it takes the vacant place between hyponitrous and nitrous acids in the series and corresponds with a hydrate of nitrogen dioxide. W. J. P.

**The Electrolysis of solutions of Ammonia containing Salts and Bases.** By SIMA M. LOSANITSCH and MILORAD Z. JOVITSCHITSCH (*Ber.*, 1896, **29**, 2436—2438). When a solution of ammonia and common salt is electrolysed in the usual Hofmann apparatus, there is always a deficiency in the nitrogen evolved. This is due to the occurrence of secondary reactions. When a chloride is present, the liquid is found to contain hypochlorite, which is either a direct product of the action of chlorine on the ammonia, or an indirect product formed by the action of water and ammonia on previously formed chloride of nitrogen. A loud explosion occurred when the graphite electrode was heated, and the authors ascribe this to the presence of chloride of nitrogen. When the formation of hypochlorite is prevented by heating the liquid, the correct ratio of nitrogen to hydrogen is obtained. When potassium bromide is used, a hypobromite is formed, and iodide of nitrogen and a hypoiodite when potassium iodide is employed. When caustic potash or potassium sulphate is added, as well as when ammonia itself in dilute solution is submitted to electrolysis, a nitrite is produced and the volume of nitrogen obtained is too small.

A. H.

**Hyponitrous Acid.** By ARTHUR R. HANTZSCH and LUDWIG KAUFMANN (*Annalen*, 1896, **292**, 317—340. Compare Abstr., 1896, ii, 520).—Silver hyponitrite is prepared by reducing sodium nitrite with sodium amalgam in strongly alkaline solution, and after removal of hydroxylamine with mercuric oxide, adding silver nitrate to the solution acidified with nitric acid; treated in this way, 20 grams of nitrite yields 2—3 grams of silver salt, and the method compares favourably with Piloty's (Abstr., 1895, i, 556), which consists in hydrolysing benzosulphydroxamic acid with 40 per cent. aqueous potassium hydroxide.

Hyponitrous acid is obtained in the solid state by adding the silver salt to ethereal hydrogen chloride until silver chloride ceases to be formed; the filtered medium is then evaporated as rapidly as possible in the desiccator, when the acid crystallises in leaflets. It is deliquescent and dissolves readily in water and alcohol; it is only sparingly soluble in petroleum, but more readily in ether, chloroform, and benzene; the crystals, when wet with ether, do not rapidly undergo change, but the dry substance explodes spontaneously, even at $-6°$. Determinations of the molecular weight, effected by adding the silver

salt to water containing a known quantity of hydrogen chloride, yield results in accordance with the formula $H_2N_2O_2$. Titration of hyponitrous acid with alkali, using phenolphthaleïn as indicator, shows that the hydrogen sodium salt, like hydrogen sodium carbonate, is neutral towards this indicator; if the solution is kept for a time at the ordinary temperature, sodium hydroxide and nitrous oxide are formed. Solutions of pure hyponitrous acid do not immediately liberate iodine from potassium iodide, but the amount of the free halogen gradually increases with time; diphenylamine develops an intense blue coloration, and if ferrous sulphate is added to concentrated sulphuric acid mixed with silver hyponitrite, the brown ring characteristic of nitrous and nitric acids is produced.

*Ammonium hyponitrite*, $H_4N{\cdot}O{\cdot}N{:}N{\cdot}OH$, is obtained by passing dry ammonia gas into a cooled solution of the acid in ether; it melts and decomposes at 64—65°, and at the ordinary temperature is resolved spontaneously into ammonia, water, and nitrous oxide. The salt dissolves readily in water, the solution being alkaline, but the aqueous and alcoholic solutions leave no residue on evaporation; normal ammonium hyponitrite has not been obtained.

*Benzylic hyponitrite*, $CH_2Ph{\cdot}O{\cdot}N{:}N{\cdot}O{\cdot}CH_2Ph$, is obtained from benzylic iodide and silver hyponitrite in ether, and crystallises from light petroleum in leaflets; it melts and evolves nitrogen at 43—45°, and explodes at 60° when rapidly heated. The salt is volatile at the ordinary temperature.

It has been generally accepted that hyponitrous acid decomposes into nitrous acid and water, but it is now established that nitrous acid and ammonia are among the products of change; it is found that hyponitrous acid is most stable in alkaline, least stable in acid, solution, an aqueous solution occupying the mean position.

Determinations of the molecular conductivity of hyponitrous acid have been made, and the results show that it is very low in a freshly prepared solution, increasing, however, with the lapse of time; in the case of the sodium salt, it is higher, and gradually decreases with time. The conductivity constant shows that hyponitrous acid is very feebly acidic, being of the same order as carbonic acid, and it is interesting to notice that the value for nitramide is even lower than that for hyponitrous acid. M. O. F.

**The Isomerism of Compounds $N_2O_2H_2$.** By ARTHUR R. HANTZSCH (*Annalen*, 1896, **292**, 340—358).—This paper does not lend itself to condensation. An attempt is made to establish a stereoisomeric relationship between the two compounds of the formula $N_2O_2H_2$, nitramide and hyponitrous acid. The author claims to have refuted Bamberger's criticisms on his views regarding the structure of diazo-salts. M. O. F.

**Nitrogen Pentasulphide.** By WILHELM MUTHMANN and A. CLEVER (*Zeits. anorg. Chem.*, 1896, **13**, 200—208).—*Nitrogen pentasulphide*, $N_2S_5$, is obtained by heating nitrogen sulphide $N_4S_4$ (Abstr., 1896, ii, 298) with pure carbon bisulphide at 100° for two hours under a pressure of five atmospheres. A deep red solution is obtained

together with a yellowish-brown, amorphous precipitate; the filtrate is distilled until the greater part of the carbon bisulphide is separated, and the residue is allowed to evaporate at the ordinary temperature in a vacuum. The red oily product, consisting of a mixture of the pentasulphide with sulphur, is triturated with perfectly dry ether as quickly as possible, when the greater portion of the sulphur remains undissolved. The residual sulphur is crystallised out by means of a freezing mixture ($-25°$) and the filtrate allowed to evaporate in dry air; finally, the last traces of ether are removed by allowing the product to remain over calcium chloride, and the residual red oil is filtered. If the product is pure and contains no sulphur, it crystallises from a well-cooled solution in ether in metallic tablets resembling iodine. A cryoscopic determination of the molecular weight, using benzene as the solvent, gave numbers agreeing with the formula $N_2S_5$. The amorphous bye-product mentioned above gave, on analysis, numbers agreeing with the formula $C_3N_3S_3$; it is a very finely divided yellow powder, is extremely hygroscopic and obstinately retains traces of carbon bisulphide and nitrogen pentasulphide. It dissolves without alteration in concentrated sulphuric acid, and has properties similar to those of pseudocyanogen sulphide, $C_3N_3S_3H$. The formation of the pentasulphide takes place according to the equation $N_4S_4 + 2CS_2 = N_2S_5 + S + 2CNS$. The pentasulphide is also formed by heating a mixture of nitrogen sulphide and carbon tetrachloride, an amorphous black bye-product being also formed containing carbon, nitrogen, sulphur and chlorine; this quickly decomposes on exposure to the air with evolution of sulphurous anhydride. It is also produced by reducing with zinc dust thiotrithiazyl chloride, $N_3S_4Cl$, suspended in methylic alcohol; and generally by the decomposition of nitrogen sulphide and its derivatives; for instance, when nitrogen sulphide is exploded by friction, when the compounds of nitrogen sulphide with the halogens, or with nitrous or nitric acid are boiled with water, and when nitrogen sulphide is heated cautiously with lead oxide. It is not, however, formed by heating nitrogen sulphide with ether or benzene at 110°—125° in a sealed tube; in this case, the greater part of the sulphide is decomposed into nitrogen and sulphur. With ether, a small quantity of a compound having an odour resembling that of acetamide is formed, and with benzene a small quantity of a compound having the characteristic odour of "oleum absynthii."

Nitrogen pentasulphide is a deep red liquid, does not wet glass, has a sp. gr. = 1·901 at 18°, is partially decomposed when distilled even under diminished pressure, solidifies in a freezing mixture to a crystalline mass resembling iodine, and melts at 10—11°. It is insoluble in water, but soluble in most organic solvents, and is stable in solution provided it is not exposed to light; in the latter case, it decomposes into nitrogen sulphide and sulphur. The pure compound quickly decomposes into nitrogen sulphide and sulphur. The absorption spectrum of the solution shows a broad band extending from the D-line into the blue. When boiled with water, a small quantity distils unchanged, but the remainder is converted into ammonia and sulphur. Alkalis decompose it completely in a similar way. When a very minute quantity

of alcoholic potash or soda is added to the alcoholic solution, an intense but transient violet-red coloration is produced, and this reaction is so characteristic that the smallest quantity of the pentasulphide can be detected. When it is added to alcoholic potash, a dark-coloured solution is obtained, from which ether precipitates a yellow, crystalline compound; this is probably a sulphonitrate, and decomposes directly it is removed from the solution. With alcoholic alkali sulphides, it yields polysulphides and ammonia, and with hydrogen sulphide ammonium polysulphide and sulphur. It is violently oxidised by concentrated nitric acid with formation of sulphuric acid; and with dilute hydrochloric or sulphuric acid, it yields ammonium salts and sulphur.

E. C. R.

**Trimetaphosphimic Acid and its Decomposition Products.** By HENRY N. STOKES (*Amer. Chem. J.*, 1896, **18**, 629—663).—A metaphosphimic acid is defined as a metaphosphoric acid $(HPO_3)_n$, in which one-third of the oxygen is replaced by an equivalent number of NH groups.

To prepare trimetaphosphimic acid (Abstr., 1895, ii, 217), the *sodium* salt, $P_3N_3O_6H_3Na_3 + 4H_2O$, is first isolated by shaking a solution of 30 grams of triphosphonitrilic chloride $(P_3N_3Cl_6)$ in 150 c.c. of ether with a solution of 110 grams of sodium acetate crystals in 200 c.c. of water; after agitation for 80 hours, the new salt will have crystallised. When formed at temperatures below 80°, the crystals are orthorhombic (measurements given), with $4H_2O$; above 80° they are microscopic flat prisms, with $1H_2O$. The salt is neutral to litmus. When it is dissolved in an excess of caustic soda solution and the liquid is concentrated, the *tetra-sodium* salt, $P_3N_3O_7H_4Na_4 + H_2O$, crystallises in long, brittle needles which are very unstable, being easily decomposed by carbonic anhydride. Salts with fewer than three or more than four sodium atoms could not be prepared.

The *potassium* salt, $P_3N_3O_6H_3K_3$, the *ammonium* salt, $P_3N_3O_6H_3(NH_4)_3 + H_2O$, the *magnesium* salt, the *barium* salt, and the *barium sodium* salt, $P_3N_3O_6H_3NaBa + 1\frac{1}{2}H_2O$ (?), are described.

The *silver* salt, $P_3N_3O_6H_3Ag_3$, is precipitated by adding silver nitrate to a solution of the sodium salt; in the presence of nitric acid, it separates slowly in the form of colourless, monoclinic plates (measurements given); it is soluble in ammonia. When the tetrasodium salt is used, and the silver nitrate is added in excess, the salt $P_3N_3O_6H_2Ag_4$ (or $P_3N_3O_7H_4Ag_4$) is formed as a white precipitate which changes into the yellow, crystalline salt, $P_3N_3O_6Ag_6$ (or $P_3N_3O_7H_2Ag_6$), when left under pure water. A red, crystalline salt of the same formula was also obtained.

Trimetaphosphimic acid is prepared by decomposing the silver salt with hydrogen sulphide; it is a gummy mass, distinguished from metaphosphoric acid in that it does not coagulate albumin. The final products of the hydrolysis of this acid are ammonia and orthophosphoric acid, but the intermediate products, diiminotriphosphoric acid, iminodiphosphoric acid, and pyrophosphoric acid, have been isolated. To separate these, advantage is taken of the insolubility of magnesium iminodiphosphate, pyrophosphate, and orthophosphate, and the solubility

of magnesium diiminotriphosphate in a feebly ammoniacal solution. The filtrate from the magnesium precipitate may be neutralised and treated with silver nitrate, to obtain silver diiminotriphosphate, from which the sodium salt may be isolated by treatment with sodium chloride. The magnesium precipitate is dissolved in dilute nitric acid, ammonia is added to the solution until incipient precipitation occurs, and then an excess of silver nitrate, whereby silver iminodiphosphate is chiefly precipitated; it must be purified by dissolving it in ammonia, reprecipitating as the magnesium salt, and repeating the process.

*Trisodium diiminotriphosphate*, $P_3N_2O_8H_4Na_3$, is precipitated in the form of microscopic, flat, pointed prisms or rhombic plates on adding alcohol to its aqueous solution; it is neutral. The *silver* salt, $P_3N_2O_8H_4Ag_3$, forms colourless, monoclinic crystals (measurements given), which are easily soluble in ammonia, but only sparingly so in dilute nitric acid. The salt, $P_3N_2O_8H_2Ag_5$, is precipitated in a white, amorphous form when an ammoniacal solution of the sodium salt is added to an excess of silver nitrate solution.

*Trisodium iminodiphosphate*, obtained by decomposing the silver salt, is precipitated by alcohol from its aqueous solution as a syrup which dries to a gummy mass; it is alkaline. *Silver iminodiphosphate*, $P_2NO_6H_2Ag_3$, is a white precipitate characterised by its granular form; the salt, $P_2NO_6HAg_4$, exists in a white and a yellow form. The *magnesium*, *ferric* and *cupric* salts are also described.

In discussing the constitution of the foregoing acids, the author expresses the opinion that Gladstone's pyrophosphodiamic acid (this Journal, 1868, 67) is trimetaphosphimic acid, and his pyrophosphamic acid iminodiphosphoric acid. Trimetaphosphimic acid probably has the constitution expressed by the formula $PO(OH){<}^{NH\cdot PO(OH)}_{NH\cdot PO(OH)}{>}NH$. Imino-diphosphoric acid and di-iminotriphosphoric acid are regarded as $PO(OH)_2\cdot NH\cdot PO(OH)_2$ and $PO(OH)_2\cdot NH\cdot PO(OH)\cdot NH\cdot PO(OH)_2$ respectively.

A. G. B.

**Compounds of Phosphorus with Selenium.** By WILHELM MUTHMANN and A. CLEVER (*Zeits. anorg. Chim.*, 1896, **13**, 191—199).—The compounds described are very similar to those of arsenic and selenium (Abstr., 1896, ii, 18). Phosphorus pentaselenide is prepared according to the method described by Bogen (*Annalen*, 1862, **124**, 57), by melting together the theoretical proportions of red phosphorus and selenium in an atmosphere of carbonic anhydride. It is most important that the materials should be thoroughly dried, as otherwise large quantities of hydrogen selenide are formed. Phosphorus triselenide is prepared in a similar way. Both compounds are unstable when exposed to the atmosphere, and absorb moisture with the formation of hydrogen selenide and the corresponding phosphorus acid. The compounds obtained by treating the phosphorus selenides with alkalis are more easily formed and crystallise better than the selenoarsenic salts; the phosphorus selenides also, unlike the arsenic selenides, are capable of forming ammonium compounds with ammonia, ammonium carbonate, and ammonium sulphide, and double salts with magnesia similar to

the compounds obtained from the sulphophosphates. The alkali carbonates decompose the phosphorus selenides whereas they do not decompose arsenic selenide.

*Potassium triselenophosphite*, $K_2HPSe_3$, $2\frac{1}{2}H_2O$, is obtained by the action of potassium hydroxide on phosphorus pentaselenide. It is more easily prepared by gradually adding the powdered triselenide to a cold concentrated solution of potassium hydroxide, cautiously warming the mixture at 75°—78° until solution takes place, and allowing the filtered solution to crystallise in a freezing mixture; if the mixture is heated above 80°, complete decomposition takes place and hydrogen selenide is evolved. It crystallises in highly lustrous octahedra-like forms, which do not, however, belong to the regular system as they show double refraction; it gradually decomposes in damp air with separation of selenium and hydrogen selenide: when heated, it gives off water vapour and hydrogen selenide, whilst selenium, and then selenious acid sublime, leaving a residue of phosphate. It is sparingly soluble in cold water, easily so in hot water, and can be recrystallised from concentrated potassium hydroxide. The aqueous solution is neutral and pale yellow. With dilute acids, it yields hydrogen selenide, and selenium is gradually precipitated. Lead and silver salts give brownish, amorphous precipitates which gradually darken, and the supernatant solution then contains phosphoric acid. Barium salts give a yellow, amorphous precipitate which quickly turns red.

*Potassium thioselenophosphite*, $2K_2S$, $P_2Se_3$, $5H_2O$, is obtained by the action of potassium sulphide on the triselenide; it forms small, colourless, doubly-refractive crystals having an octahedral habit and an adamantine lustre, and is decomposed at about the same temperature as the preceding salt with evolution of hydrogen sulphide and selenide. The aqueous solution is colourless, and when treated with acids yields hydrogen sulphide and selenide, whilst a reddish-brown compound mixed with sulphur is precipitated. When treated with salts of the heavy metals, it yields dark, amorphous precipitates.

*Sodium oxyselenophosphate*, $Na_3PSe_3O + 10H_2O$, is obtained by the action of sodium hydroxide on the triselenide in a similar way to the potassium salts just described. It crystallises from concentrated sodium hydroxide in pale green, doubly-refracting prisms. The aqueous solution quickly decomposes; with acids, it yields hydrogen selenide and a brown precipitate containing selenium. When heated in a tube, it yields a sublimate of selenium, and a phosphate.

All the above substances give well crystallised compounds with ammonia magnesia mixture. E. C. R.

**Boric Acid and its Salts.** By LOUIS KAHLENBERG and OSWALD SCHREINER (*Zeits. physikal. Chem.*, 1896, 20, 547—568).—The determination of the molecular depressions due to solutions of boric acid and its salts, lead to the conclusion that in aqueous solution only the one boric acid exists, namely $H_3BO_3$, and this is formed if the anhydride or a partial anhydride is dissolved. A solution of borax is identical with the solution containing equivalent quantities of boric acid and sodium hydroxide. By the determination of the conductivity and of

the E.M.F. of borate chains, the number of ions present in the solutions was determined, and the conclusions arrived at are that in concentrated solutions of borax there are present sodium ions and anions containing 2 atoms of boron. These anions are, by dilution, dissociated so that in dilute solutions sodium ions and anions containing 1 boron ion are present, and also undissociated boric acid. A solution of sodium metaborate is identical with a solution of boric acid with the equivalent quantity of sodium hydroxide, or to borax solution with sodium hydroxide; the solution contains very few hydroxyl ions and is only slightly decomposed by water. By the addition of more sodium hydroxide, only small quantities of higher compounds are formed, since almost the calculated excess of hydroxyl ions are found in the solution.

The nature of the reaction of borates with polyvalent alcohols was also investigated. The addition of 2 molecules of mannitol to 1 molecule of borax in solution has little effect on the freezing point depression, which is increased by further addition of mannitol; it, moreover, causes the solution to become acidic. If the solution contains sodium hydroxide as well as borax, the addition of mannitol at first decreases the depression, and the results are best explained on the assumption of the formation of a complex anion containing 2 boron atoms and 1 molecule of mannitol, which on adding more of the latter yields an anion containing 2 boron atoms and 2 mannitol molecules; no further combination, however, occurs, so that after this stage is reached the depression is increased. The effects of the addition of mannitol, erythritol, glycerol, and glycol on the electrical conductivity of solutions of borax were also determined, and diagrams representing the results are given. These effects further support the freezing point evidence of the formation of complex ions. L. M. J.

**Attempt to Liquefy Helium.** By KARL OLSZEWSKI (*Ann. Phys. Chem.*, 1896 [2], **59**, 184—192).—Helium from clèveite of density 2·133 from which all gases that are absorbed by magnesium, copper oxide, phosphoric anhydride and caustic soda had been removed, was cooled down by boiling ethylene and afterwards by boiling air first to $-150°$ and then to $-220°$. It was submitted at the lower temperature to a pressure of 140 atmospheres and the pressure then suddenly reduced to 20 atmospheres, but the gas showed no sign of liquefaction. With the help of the well-known equation $T/T_1 = (p/p_1)^{\frac{k-1}{k}}$ the author calculates the boiling point of helium as below $-264°$, or at least 20° lower than that of hydrogen. The monatomic character of the helium molecule probably accounts for the fact that this gas although of greater density than hydrogen has the lower boiling point.

A comparison of the helium and hydrogen thermometers for temperatures between $-182°$ and $-210°$ shows a very fair agreement, and that therefore the coefficient of expansion of hydrogen remains the same even at these low temperatures. H. C.

**Combination of Argon with Water.** By P. VILLARD (*Compt. rend.*, 1896, **123**, 377—379).—When carefully purified argon is compressed at 150 atmospheres in presence of water cooled to about 0°, and the water is

further cooled so that it solidifies at one point, combination takes place between the gas and the water with production of a crystalline hydrate similar to those formed by many other gases. Mere compression of the gas in presence of water is not sufficient, but the presence of previously formed crystals of the hydrate has the same effect as the freezing of a small quantity of the water.

The tension of dissociation of the hydrate is 105 atmospheres at 0° and 210 atmospheres at 10°. C. H. B.

**A form of Silver obtained on the Reduction of the Sulphide by Hydrogen.** By FRANCIS C. PHILLIPS (*J. Amer. Chem. Soc.*, 1894, **16**, 700—703).—If silver chloride is heated in hydrogen to 300°, reduction occurs, and the metallic silver appears as a compact, rounded mass having a moderate lustre. Precipitated silver sulphide when heated to temperatures above 450° in hydrogen, is reduced and the dull black powder gradually changes into a mass of tangled wires or threads which exhibit the lustre of highly polished silver. The wires vary in thickness from that of the finest hairs to that of coarse sewing-thread; and they are often so knotted and linked together as to be almost inextricable. Argentite behaves in a similar manner, but stephanite, $Ag_5SbS_4$, yields no silver even when heated in hydrogen to dull redness. Artificial copper sulphide when slowly reduced at about 600° yields lustrous threads of copper resembling those obtained in the case of silver. Compare Opificus (*Chem. Zeit.*, 1888, 649), Bischof (*Annalen*, 1843, 289), and Hampe (*Chem. Zeit.*, 1893, 1692).

J. J S.

**Oxidation of Silver.** By CHARLES E. WAIT (*J. Amer. Chem. Soc.*, 1896, **18**, 254—259).—The author has previously drawn attention to the fact that a certain bismuth litharge from a Western smelting company contained a large amount of silver (2·94 per cent.). It was also shown that the silver was not in the metallic state but was probably present as the oxide, since it readily dissolved in warm acetic acid. In order to account for the formation of the silver oxide, the author has studied the action of various metallic oxides on silver at fairly high temperatures. He finds that manganese dioxide readily oxidises metallic silver to the oxide. Experiments have shown that, other conditions being equal, the longer the duration of the heating the less silver oxide is formed. 0·5 gram of silver, and 2 grams of manganese dioxide, when heated for 2·5 mins., gave 34·28 per cent. of the silver in the form of oxide, but when heated for 20 mins. gave only 11·72 per cent.

Oxides of iron, bismuth, copper and zinc cannot bring about this oxidation, but lead monoxide and dioxide and barium peroxide can. The lead monoxide no doubt acts as an oxygen carrier, and the presence of silver oxide in certain litharges is to be attributed to the oxidising influence of the litharge. J. J. S.

**Hydraulic Cements.** By ORAZIO REBUFFAT (*Gazzetta*, 1896, 26, ii, 242—244).—The author replies to Oddo's criticisms (Abstr., 1896, ii, 246). W. J. P.

**Atomic Weight of Magnesium.** By THEODORE W. RICHARDS and H. G. PARKER (*Zeits. anorg. Chem.*, 1896, **13**, 81—100).—The methods employed consist in determining the weight of silver chloride obtained by precipitating a known weight of magnesium chloride with excess of silver nitrate: also by precipitating a known weight of magnesium chloride with the calculated quantity of pure silver dissolved in nitric acid and then by means of two equivalent solutions of silver and ammonium chloride (the silver solution = 1 milligram per c.c.) determining the point at which equal addition of the two equivalent solutions produces an equal turbidity in the clear supernatant liquid. This point is determined by means of a nephelometer and the method is delicate enough to indicate the difference between 0·002 and 0·003 milligram of silver chloride. All the operations of precipitation, &c., are performed in orange-coloured light.

Pure magnesium chloride free from water, oxychloride or ammonium chloride is obtained by heating magnesium ammonium chloride contained in a platinum boat in a current of perfectly dry hydrogen chloride, at first cautiously, so as to remove any water that may be present: the temperature is then raised and the ammonium chloride volatilised, finally the magnesium chloride is heated to redness until it melts to a clear, colourless liquid. It is then cooled in a current of dry nitrogen, and when cold, the nitrogen is displaced by a current of dry air; the pure dry magnesium chloride is transferred to a weighing bottle without removing it from the drying apparatus. A full description, with drawings of the apparatus, is given in the original paper. The greatest care must be taken to exclude every trace of moisture, as otherwise oxychloride is formed.

The following results were obtained. Series I. (5 experiments) the ratio $2AgCl : MgCl_2$ gave Mg = 24·369. Series III. (6 experiments) the ratio $2Ag : MgCl_2$ gave Mg = 24·365. Series IV. (6 experiments) the ratio $2Ag : MgCl_2$ gave Mg = 24·362. The individual results of Series IV. agree extremely well with one another, the greatest difference amounting to only one-tenth of a milligram of magnesium chloride. Hence the authors accept the last value as the probable atomic weight of magnesium; this compared with the atomic weight of oxygen gives O = 16. Mg = 24·362 : O = 15·96, Mg = 24·301 : O = 15·88, Mg = 24·179.

E. C. R.

**Magnesium Nitride.** By A. SMITS (*Rec. Trav. Chim.*, 1896, **15**, 135—137. Compare Abstr., 1894, ii, 16).—When an intimate mixture of magnesium nitride, $Mg_3N_2$, and anhydrous nickel chloride is heated gently in a sealed tube, a brisk reaction takes place; the product after washing with warm water forms a black mass which, when dissolved in mineral acids, yields a green solution, containing ammonia; the black compound is therefore, probably, a nitride of nickel. Anhydrous ferrous, ferric, and cobalt chlorides behave in a somewhat similar manner, except that the black compounds formed are free from nitrogen. Chromic chloride yields a nitride, CrN, which is not acted on by acids at the ordinary temperature; this forms small black plates.

Mercuric chloride yields a green nitride of mercury which is decomposed by acids. Silver nitrate gives a yellow silver nitride which is decomposed by water, yielding silver oxide and ammonia. Platinic chloride when heated with magnesium nitride, even at a low temperature, yields metallic platinum. Cupric oxide or sulphate yields a greenish yellow nitride or at higher temperatures metallic copper. Lead peroxide and the oxides of iron also react vigorously with magnesium nitride. J. J. S.

**Corrosion Phenomena of Zinc Plates.** By FRANZ MYLIUS and ROBERT FUNK (*Zeits. anorg. Chem.*, 1896, 13, 151—156).—Cast zinc and cadmium anodes which are contaminated with a layer of oil or grease, when subjected to a current of 1 ampère per square decimetre in a bath of zinc sulphate, are pitted and the skin is undermined by the action of the electric current in such a way that a thin skin is separated. Rolled zinc plates suffer a like corrosion, which is probably due to the mixing of the impurities contained in the zinc by the process of rolling. The corrosion of zinc containing lead is hindered by sudden cooling when cast and by the mechanical treatment of rolling. The mechanical treatment of pure zinc has, however, a very slight influence on the ease with which corrosion takes place. An analysis of the outer skin and the inner layer of a commercial zinc plate gave practically the same percentage composition, so that the corrosion phenomena cannot be due to a difference in the composition of the outer skin. E. C. R.

**Zinc Carbonate.** By KARL KRAUT (*Zeits. anorg. Chem.*, 1896, 13, 1—15).—The author has determined the composition of the products obtained by precipitating zinc salts with alkali carbonates, and hydrogen carbonates under varying conditions. The first product obtained when solutions of these salts are poured into solutions of zinc sulphate is normal amorphous zinc carbonate. This, according to circumstances, is then either converted into the stable crystalline zinc carbonate, $ZnCO_3,H_2O$, or into the basic carbonate, $5ZnO,2CO_2,4H_2O$, with evolution of carbonic anhydride. The basic zinc carbonate, $2ZnO,CO_2$, described by Boussingault, Wackenroder, and H. Rose, and probably all the basic carbonates having compositions between the compounds $ZnO,CO_2$ and $5ZnO,2CO_2$, are mixtures formed by the partial conversion of the primary amorphous zinc carbonate into crystalline carbonate and into the basic carbonate, $5ZnO,2CO_2,4H_2O$. If the solution of the zinc salt is added to a solution of alkali carbonate, the normal carbonate is not formed, but only the basic carbonate, and this is due to the presence of an excess of alkali carbonate during the precipitation. Finally, the basic carbonate, when boiled with excess of alkali carbonate, is converted into anhydrous zinc oxide.

Basic zinc carbonate, $5ZnO,2CO_2,4H_2O$, can be obtained pure by dissolving zinc, hydrated zinc oxide, or zinc carbonate in an excess of aqueous carbonic acid and then boiling the solution, when it is precipitated. It is also obtained very nearly pure by precipitating zinc sulphate with an alkali carbonate from cold dilute solutions or from boiling solutions, if equivalent quantities of both salts are em-

ployed. Concentration of the solutions determines the formation of the normal carbonate, and dilution, the formation of the basic carbonate; above a certain concentration, excess of potassium or sodium hydrogen carbonate combines with the zinc carbonate to form double salts.

A solution of zinc sulphate in water was mixed with a solution of sodium hydrogen carbonate in water, in the proportion $ZnSO_4$ : $4NaHCO_3$; the precipitate was allowed to remain under the mother liquor until it had become crystalline, then collected, and washed with a solution of sodium hydrogen carbonate. It consisted of small quadratic optically active crystals of zinc carbonate, $ZnCO_3,H_2O$, and of larger octahedral skeleton forms which were inactive, and gave on analysis numbers agreeing with the formula $Na_2O,3ZnO,4CO_2,3H_2O$. The two compounds can easily be separated mechanically.

The author was unable to prepare a basic carbonate of cadmium. Only a very small quantity of cadmium carbonate is dissolved by aqueous carbonic acid, even under a pressure of several atmospheres. The precipitate obtained by adding cadmium sulphate to a solution of sodium carbonate consists of cadmium carbonate, $CdCO_3$, mixed with a small quantity of the basic sulphate, $2CdO,SO_3$; whilst by adding cadmium nitrate to an excess of ammonium carbonate, the carbonate $CdCO_3 + \frac{1}{2}H_2O$ is obtained. E. C. R.

**Electrolytic Refining of Cadmium.** By FRANZ MYLIUS and ROBERT FUNK (*Zeits. anorg. Chem.*, 1896, 13, 157—160).—The electrolytic refining of cadmium is carried out in a very similar way to that of zinc. The cadmium is deposited from a concentrated solution of cadmium sulphate, slightly acidified, on cathodes of platinum or cadmium foil, a current density of 0·5—1 ampère per square decimetre being employed. The deposited cadmium is easily separated from the cathodes, and when melted and sublimed in a vacuum is obtained in flat needles or silvery six-sided tablets. No impurities can be detected by chemical means in the metal so prepared.

The lead in the impure metal is completely separated by electrolysis of the sulphate solution with a very weak current, and is deposited partly at the cathode as metal and partly at the anode as peroxide. Iron is most easily detected by means of potassium thiocyanate. The presence of zinc is detected by melting a sample of the metal in a porcelain crucible and breaking the skin of oxide with a glass rod, so that the bright molten metal is exposed; if the cadmium is free from zinc, the bright surface in a few seconds becomes covered with a many-coloured oxidation skin; in the presence of zinc, however, the oxidation of the cadmium is hindered, and zinc oxide is first formed. This reaction is so delicate that less than 0·01 per cent. of zinc can be detected.

The quantitative estimation of the zinc in cadmium is effected by transferring the cadmium electrolytically through a very dilute acid or salt solution, whereby the whole of the zinc remains in solution together with a small quantity of cadmium, and can now be easily separated from the latter. E. C. R.

**Crystallised Slags from Copper-smelting.** By ALFRED C.

LANE (*Bull. Geol. Soc. Amer.*, 1895, **6**, 469—470).—At the smelting works at Dollar Bay and on Torch Lake in Upper Michigan, the copper which has been oxidised during the melting down of the ore is afterwards reduced. The slag produced in this reduction has a strong tendency to crystallise, and contains very large melilite crystals in the form of square tablets with rounded and reticulated faces. The crystals are optically uniaxial and negative; they are merely shells, with a rectangular network of enclosed matter, consisting of a greenish birefringent substance, iron oxides, and globules of copper; a partial analysis, by R. L. Packard, gave

| $SiO_2$. | $Fe_2O_3$. | $Al_2O_3$. | CaO, MgO, &c. [diff.]. |
|---|---|---|---|
| 34·84 | 16·78 | 13·26 | [35·12] |

In cavities in the slag are small scales of hæmatite. L. J. S.

**Solubility of Lead and Bismuth in Zinc.** By WALTHÈRE SPRING and L. ROMANOFF (*Zeits. anorg. Chem.*, 1896, **13**, 29—36).—A crucible is prepared with a hole bored in the side at a convenient distance from the bottom and stopped with a plug during the preparation of the solution. The crucible is filled with the heavier metal (lead or bismuth) so that the level of the molten metal is just above the hole, the zinc is then added, covered with a protecting layer of fused salt or charcoal, and the crucible maintained at the temperature at which the solubility is to be determined. The contents are stirred about every 10 minutes. The sample of the top layer is taken by bailing out a sufficient portion. The plug is then knocked out of the side of the crucible, and after the top layer has run out, a sample of the bottom layer is bailed out. A table of the composition of the two layers at temperatures from 266—900° is given. When the results are stated graphically, taking the temperature for abscissæ and the percentage of the two layers as ordinates, two points are obtained for each temperature: one the solubility of bismuth in zinc, the other the solubility of zinc in bismuth, and by prolonging these two until they meet, the temperature is determined at which the two metals will mix in all proportions. The critical temperature for bismuth and zinc lies between 800—850°, that for lead and zinc between 900—950°. The curves are analogous to those obtained by Alexéeff for non-miscible liquids. E. C. R.

**Metaplumbates.** By M. HOEHNEL (*Arch. Pharm.*, 1896, **234**, 397—400).—Calcium metaplumbate (Abstr., 1896, ii, 248) is much more stable than the metaplumbates of sodium and potassium; by digesting it with a solution of the acetate of a heavy metal, the metaplumbate of that metal can be prepared. The following were obtained in this way: *metaplumbate* of *zinc*, $ZnPbO_3 + 2H_2O$, reddish-brown, crystalline; of *copper*, $CuPbO_3$, black, amorphous; of *manganese*, grey-black, crystalline; of *lead*, $PbPbO_3$, reddish-brown, amorphous, and identical with lead sesquioxide. C. F. B.

**Potable Waters which have flowed through Lead Pipes.** By UBALDO ANTONY AND T. BENELLI (*Gazzetta*, 1896, **26**, ii, 97—107, 352—362).—The authors have examined the action of water of various

degrees of purity on lead, and have obtained analytical results which are summarised in the accompanying table.

| | Parts of lead per 100,000. | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| Water alone, unfiltered | 8·19 | 12·98 | 8·19 | 4·09 |
| Water alone, filtered | 3·00 | 4·09 | 2·07 | 2·32 |
| Water containing chlorides, unfiltered | 1·36 | 2·73 | 0·68 | 4·09 |
| Water containing chlorides, filtered | 0·68 | 1·50 | 0·67 | 1·36 |
| Water containing sulphates, unfiltered | 3·41 | 6·83 | 2·05 | 1·84 |
| Water containing sulphates, filtered | 2·05 | 3·41 | 1·64 | 1·77 |

Water was allowed to remain in contact with lead wire for five days, each 150 c.c. of water being in contact with 285 square cm. of metal. The amount of lead in the unfiltered and filtered water was then determined. The column headed 1 gives the numbers for distilled water free from air,—first for the pure water, then for water containing 0·049 gram of sodium chloride per litre, and finally for water containing 0·49 gram of sodium sulphate per litre; column 2 gives the corresponding data for distilled water aërated by agitation with air; column 3 shows the results obtained with water continuously aërated by passing 1 litre of air through it per hour, whilst column 4 gives the data for distilled water through which 1 litre of air and 400 c.c. of carbonic anhydride were passed per hour throughout the experiment. The lead was determined by the process previously described by the authors (Abstr., 1895, ii, 549).

The authors next experimented on the solubility of lead in water containing various dissolved substances, with the results summarised in the accompanying table.

| Water used. | Parts of lead per 100,000. | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| Distilled water alone | 8·19 | 12·98 | 8·19 | 4·09 |
| Distilled water with NaCl | 1·36 | 2·75 | 0·68 | 4·09 |
| Distilled water with $Na_2SO_4$ | 3·41 | 6·83 | 2·05 | 1·84 |
| $CaHCO_3$ solution alone | 2·45 | 3·14 | 2·63 | 5·70 |
| $CaHCO_3$ solution with NaCl | 2·05 | 3·41 | 2·35 | 3·40 |
| $CaHCO_3$ solution with $Na_2SO_4$ | 2·18 | 3·32 | 2·05 | 3·16 |
| $CaSO_4$ solution alone | 6·83 | 6·83 | 3·41 | 1·35 |
| $CaSO_4$ solution with NaCl | 5·46 | 6·57 | 3·51 | 1·50 |
| $CaSO_4$ solution with $Na_2SO_4$ | 4·78 | 5·87 | 3·69 | 1·77 |

The experiments were conducted under conditions similar to those prevailing in the earlier experiments. Columns 1, 2, 3, and 4 refer to the solutions named in the first column (1) free from air; (2) saturated

with air; (3) continuously aërated by a current of air; and (4) continuously aërated by a current of air and carbonic anhydride; the quantities of sodium chloride and sulphate present in the various samples of water were the same as before. In the experiments with solutions of calcium hydrogen carbonate, each litre contained 0·04 gram of CaO as carbonate, whilst in the tests with calcium sulphate, each litre of water contained 0·095 gram of CaO as sulphate. W. J. P.

**Double Chlorides.** By RAOUL VARET (*Compt. rend.*, 1896, **123**, 421—423).—The double chlorides formed by mercuric chloride $2HgCl_2,MCl_2 + nH_2O$, and $HgCl_2,MCl_2 + nH_2O$ are all more or less dissociated when their solutions are submitted to dialysis. The author finds that when dilute solutions of mercuric chloride and various metallic chlorides are mixed, there is a development of heat which varies in different cases from 0·80 to 1·36 Cal., but generally approximates somewhat closely to 1·0 Cal. The double salts may be regarded as derived from two complex unstable acids, $H_2HgCl_4$ and $H_2Hg_2Cl_6$.

Solutions of cupric or cadmium chloride give practically no thermal disturbance when mixed with solutions of other metallic chlorides, and when solutions of the double chlorides of copper or cadmium are dialysed, the proximate constituents can be completely separated. It follows that these double salts exist as such in the solid state only.

C. H. B.

**The Components of Monazite.** By G. PAUL DROSSBACH (*Ber.*, 1896, **29**, 2452—2455).—The monazite examined came from the Blue Mountains. It was finely powdered, and then decomposed with sulphuric acid; from the solution, the thorium was separated by fractionation, and then a large excess of sulphuric acid was added. The erbium metals remain in solution, whilst the cerium metals are precipitated; their precipitation is rendered more complete by partially neutralising the liquid with soda, for with sodium sulphate, they form double salts which are quite insoluble in a saturated solution of that salt.

The solution of the cerium metals is then treated with potassium hydroxide and permanganate, which precipitates the cerium as the dioxide, together with some of the didymium; the latter is extracted, with dilute nitric acid: strong nitric acid then extracts the cerium, leaving the manganese dioxide. The lanthanum and didymium in solution are converted into nitrates, and these are fractionally precipitated with sodium hydroxide; didymium is first precipitated, as the basic nitrate, whilst the lanthanum remains in solution. Perhaps the two didymium precipitates obtained contain different elements.

The erbium elements in solution are precipitated with oxalic acid; the oxalates are converted into the hydroxides, and these into the nitrates, which are then fractionally precipitated with magnesia. Yttrium remains in solution; from the precipitate, ytterbium can first be separated by the basic nitrate method, and erbium next fractionally precipitated with dilute sodium hydroxide, when the solution is found

to contain what is possibly a new element, with an atomic weight in the neighbourhood of 100. C. F. B.

**Analyses of Steel.**—By GIOVANNI GIORGIS and UGO ALVISI. (*Gazzetta*, 1896, **26**, ii, 167—178).—The authors have analysed a number of specimens of soft steel, the mechanical properties of which have been studied by Biadego (*Rivista Tecnica L'Industria*, 1895, **47**, **52**; 1896, **2**, **6**, **7**). W. J. P.

**Steel.**—By FRANZ MYLIUS, FRITZ FOERSTER and GEORG SCHOENE (*Zeits. anorg. Chem.*, 1896, **13**, 38—58).—*Iron Carbide in Steel.*—The iron carbide was at first extracted from tool-steel by electrolysis. Anodes of steel plates or rods are subjected to a current of 1 ampère per quarter-decimetre in a bath of concentrated zinc sulphate containing 0·1 per cent. of free acid. The electrolysis proceeds without any appreciable evolution of hydrogen, but the anode becomes coated with a grey skin which must be occasionally rubbed off. The residue obtained consists of a grey powder which contains from 7 to 9 per cent. of carbon and about 90 per cent. of iron. It is not, however, pure carbide; for whilst the steel dissolves completely in hot hydrochloric acid, this residue contains a small quantity of insoluble carbonaceous material. The carbide was also extracted with twice normal, and with normal sulphuric acid at the ordinary temperature, washed as quickly as possible with water, alcohol, and finally with ether, and dried at 120° in a current of hydrogen, care being taken to exclude air as much as possible during the operations. Four experiments with the same steel gave products which contained from 6·5 to 7·2 per cent. of carbon, and were not completely soluble in hot hydrochloric acid, but yielded a small carbonaceous residue; this residue is formed by the oxidation of the damp carbide on exposure to air. In order to obtain an iron carbide completely soluble in hydrochloric acid, the steel is extracted on a filter bed of asbestos with sulphuric acid in an apparatus so arranged that the extraction is performed in an atmosphere of hydrogen. The residue is washed in the same apparatus with water, alcohol, and ether in an atmosphere of carbonic anhydride, and dried at 100° in a current of carbonic anhydride. This product is almost completely soluble in hydrochloric acid; the residue, which amounts to 0·1 per cent., consists of silica. It gave on analysis—6·5 per cent. C, 91·96 per cent. Fe, 1·1 per cent. Mn, 0·23 per cent. Cu, 0·02 per cent. Si, and traces of sulphur, phosphorus, arsenic and nickel. When heated to redness in a current of nitrogen or hydrogen, it lost only 0·4 per cent. in weight.

*Iron carbide*, when dry, is not altered by exposure to air. When dried at 100° in a current of hydrogen, and then exposed to air, it glows and yields iron oxide; the same phenomenon occurs occasionally when it is dried at a low temperature in carbonic anhydride or nitrogen. When heated to redness in hydrogen, it is not pyrophoric; but the hydrogen must be completely displaced by carbonic anhydride or nitrogen to render it stable on exposure to air. When damp, it is rapidly oxidised on exposure to air, yielding a brown powder, which consists of a mixture of oxide of iron and the carbon compound $C_{12}H_6O_3$ described by

Bourgeois and Schützenberger (this Journal, 1875, 788) and by Zabudzky (Abstr., 1882, 427, 660). This compound is most easily obtained by treating the carbide with a solution of ammonium sulphate in dilute sulphuric acid. The carbide is only slightly decomposed when heated with water at 145°, but when heated at 400° to 430° in a current of steam and nitrogen for half an hour, it increases 13 per cent. in weight and yields a black residue containing oxides of iron and free carbon together with a combustible gas consisting for the most part of hydrogen. When heated at a red heat in a current of steam for half an hour, it increases 29 per cent. in weight, yields a black powder of ferrosoferric oxide and a gaseous mixture of hydrogen, carbonic oxide and carbonic anhydride. It is not appreciably attacked by very dilute acids; when treated with one-tenth normal hydrochloric acid at 80°, a distinct evolution of hydrogen is observed. It is very gradually dissolved by normal hydrochloric acid, and 1 gram after remaining sealed up in a vacuum tube for 10 days with normal hydrochloric acid gave only 2·5 c.c. of a combustible gas. In concentrated hydrochloric acid, it is easily soluble and leaves only a minute residue which is insoluble in water, but easily soluble in alcohol or ether. In no case did the authors observe the formation of amorphous intermediate carbonaceous products during the dissolution. An analysis of the gas evolved on dissolving the carbide in hydrochloric acid gave 92·3 per cent. H, 6·3 per cent. hydrocarbons, 1·4 per cent. N. The ratio of the combined hydrogen to the carbon very nearly approaches that required for a member of the series $C_nH_{2n+2}$ and the density of the hydrocarbon is about the same as that of pentane. Although the iron carbide is not altered by heating to redness, it melts at a white heat in an atmosphere of nitrogen, and carbon is deposited. The cast iron regulus thus obtained contains 4·36 per cent. of carbon; it is very brittle, shows a radial fracture like that of "spiegeleisen," and contains no graphite.

In order to prove that the iron carbide is present in the steel as a definite chemical compound, the authors extracted samples of the steel with various acids of different strengths. Normal acetic acid yielded the best results, over 90 per cent. of the carbon present in the steel being obtained as carbide; whilst with $N \times 4$ hydrochloric acid only 25 per cent. of the carbide was obtained. The product, in all cases, contained the same percentage of carbon. Samples prepared from different sorts of steel gave the same composition on analysis as did also a sample prepared from carbonised iron, made in the laboratory from pure electrolytic iron which was carbonised by means of pure acetylene.

It is evident from the above results that the carbide is a definite chemical compound of the formula $Fe_3C$. Only in one reaction does it show a behaviour different from that which one would expect from a compound of the formula $Fe_3C$, which should decompose when treated with acids according to the equation $Fe_3C + 6HCl = 3FeCl_2 + CH_4 + H_2$.

E. C. R.

**Crystallised Martin-slag.** By A. Harpf (*Jahrb. f. Min.*, 1896, ii, Ref. 37; from *Österr. Zeits. f. Berg- und Hüttenwesen*, 1895, No. 7).—

Crystallised slag from the Martin-furnace at the iron and steel works at Donawitz, gave the following results on analysis :—

| $SiO_2$. | FeO. | $Al_2O_3$. | MnO. | CaO. | MgO. | Fe. | Total. | sp. gr. |
|---|---|---|---|---|---|---|---|---|
| 30·75 | 60·23 | 2·07 | 5·10 | 1·30 | 1·10 | 0·07 | 100·62 | 4·280. |

This shows the material to be fayalite. Some of the crystals are tabular, others are columnar; they show the forms *b* {010}, *c* {001}, *d* {110}, *s* {102}, and *z* {104}. L. J. S.

**New Cobalt and Nickel Salts.** By NAGENDRA CH NÂG (*Zeits. anorg. Chem.*, 1896, **13**, 16—18. Compare Durrant, Proc., 1896, 96 and 244).—When precipitated, cobalt carbonate is treated with bromine in presence of potassium hydrogen carbonate, carbonic anhydride is evolved, and a green solution is formed, from which a green compound, which does not contain bromine, is precipitated by shaking the solution with alcohol and ether. The new compound is very unstable and has not yet been isolated, but it appears to be an oxidation product probably corresponding to the ferates. A nickel compound was not obtained under like conditions.

When either cobalt or nickel carbonate is treated with sodium acetate and bromine, a deep orange-red solution is obtained. The nickel solution when boiled gives a violet precipitate and a neutral apple-green solution. The cobalt solution gives no precipitate when boiled. These orange-red compounds appear to be lower oxidation products, for when potassium hydrogen carbonate is added to the brown cobalt salt solution containing an excess of bromine, the green solution is obtained. E. C. R.

**Constitution of Cobalt, Chromium and Rhodium Bases.** By SOFUS M. JÖRGENSEN (*Zeits. anorg. Chem.*, 1896, **13**, 172—190; see also Abstr., 1895, ii, 47; 1896, ii, 424).—The author has determined the relative quantities of the compounds formed in the preparation of Erdmann's cobalt triamine nitrite (*J. pr. Chem.*, 1866, **97**, 412), and gives a table of the results. Cobalt carbonate (10 grams) dissolved in hydrochloric acid (50 c.c.), was treated with varying quantities of sodium nitrite and 20 per cent. ammonia and the mixture oxidised in various ways; the dark brown liquor obtained, was filtered from the insoluble matter and evaporated to dryness in a draught. The residue was dissolved in 50—70 c.c. of cold water, whereby a second residue was obtained, and a dark brown solution which, when treated with dilute nitric acid, yielded the xantho-nitrate. The insoluble residues were washed with cold water until free from chlorine, whereby the croceo- and xantho-chlorides were removed, and the residue free from chlorine was extracted with hot water containing some acetic acid, when the triamine nitrite was dissolved. This was separated from the croceo-diamine nitrite and other sparingly soluble impurities by fractional crystallisation from very dilute acetic acid; the bulk of the croceo-diamine nitrite was obtained in the last extraction of the residues. The last two salts are more soluble the more concentrated the acetic acid used. Of the salts of the composition $Co(NH_3)_3(NO_2)_3$, only the ordinary triamine nitrite and the croceo-diamine nitrite were obtained.

The best yield of these salts, amounting to one-fourth of the cobalt used, is obtained by employing 27 grams of sodium nitrite and 200 c.c. of 20 per cent. ammonia and passing air through the mixture for two hours and then allowing the mixture to remain for 3 days in an open dish. The relative quantities of the materials employed, the dilution, and especially the method in which the oxidation is effected, have a great influence on the composition of the products obtained.

*Different forms of the triamine nitrite and the dinitrotriamine chloride.*—The triamine nitrite crystallises, according to the conditions, in needles or in rhombic tablets. The dinitrotriamine chloride crystallises in quadratic tablets, in octahedra, in elongated prisms and in other forms; all these modifications when precipitated with hydrochloric acid are converted into quadratic tablets. The dinitrotriamine chloride is dissociated when dissolved in water, but only to a small degree at the ordinary temperature: when heated with water containing a few drops of acetic acid on the water bath, it yields the triamine nitrite according to the equation

$$2(NO_2)_2Co(NH_3)_3Cl = (NO_2)_2Co(NH_3)_3NO_2 + Co(NH_3)_3(NO_2)Cl_2.$$

The author was unable to obtain an isomeric triamine nitrite by adding sodium nitrite to the solution, and the only compound isolated was ammonium cobalt dinitrite.

*Action of dilute acids on croceocobalt-diaminecobalt nitrite.*—Croceocobalt-diaminecobalt nitrite is converted by prolonged treatment with hydrochloric acid at the ordinary temperature into a dark brown crystalline powder which consists of the chloronitro-tetramine chloride and *chloronitrotetraminecobalt-diaminecobalt nitrochloride*,

$$NO_2CoCl(NH_3)_4Cl_2(NH_3)_2Co(NO_2)_2.$$

The latter salt is separated by washing the precipitate with water, in which it is insoluble: it is then washed with alcohol (95 per cent.), dried over sulphuric acid, and purified by dissolving it in water and precipitating with hydrochloric acid. When heated with sodium nitrite, it is quantitatively reconverted into the croceodiamine nitrite. The above constitution is proved by the following reactions. When heated with hydrochloric acid, it yields the chloronitrotetramine chloride, and with dilute nitric acid, the aquoxantho-nitrate. When treated with water containing acetic acid, it yields aquoxantho-salts. Silver nitrate precipitates all the chlorine as silver chloride. When heated with water, ammonium nitrate and ammonia, it yields xanthonitrate and flavonitrate. It is also obtained by mixing a solution of the chloronitrotetramine chloride in water containing a small quantity of acetic acid with a solution of the ammonium-diamine nitrite in water and hydrochloric acid. E. C. R.

**Action of Chromic Acid on Thiosulphuric Acid.** By ANTONIO LONGI (*Gazzetta*, 1896, **26**, ii, 119—141).—In view of the fact that Longi and Bonavia (Abstr., 1896, ii, 625) have shown Diehl's interpretation of the reaction between a chromate and a thiosulphate to be erroneous, the author has examined the reaction in detail. On adding a mineral acid and potassium dichromate to a dilute sodium thiosulphate

solution, the reaction which takes place is in accordance with the equation $2H_2CrO_4 + 6H_2S_2O_3 = 3H_2S_4O_6 + Cr_2(OH)_6 + 2H_2O$, small quantities of sulphuric acid being simultaneously formed in accordance with a secondary reaction expressed by the following equation, $3H_2S_4O_6 + 14H_2CrO_4 + 16H_2O = 12H_2SO_4 + 7Cr_2(OH)_6$. Hydrogen sulphide is also produced, and it is shown that both sodium thiosulphate and tetrathionic acid give this gas when small quantities of an acid or a chromic salt are added to their solutions; more hydrogen sulphide is obtained at high than at low temperatures, and tetrathionic acid is more stable than the thiosulphate, for sodium thiosulphate gives hydrogen sulphide when treated with hydrogen peroxide or acetic acid, or when carbonic anhydride is passed through its hot solution.

W. J. P.

**Formation of Antimony Cinnabar.** By JOHN H. LONG (*J. Amer. Chem. Soc.*, 1896, **18**, 342—347. Compare Abstr., 1895, ii, 399).—It has been previously shown that antimony cinnabar, obtained by boiling a solution of antimony chloride or tartrate with sodium or calcium thiosulphate, has the composition $Sb_2S_3$.

On boiling solutions of antimony salts with hydrogen sulphide or an alkali sulphide and sulphurous anhydride, the amorphous sulphide mixed with free sulphur is always formed. A thiosulphate precipitates the cinnabar red product from either acid or neutral solutions of antimony salts, the addition of a few drops of ammonia, however, prevents the precipitation. Antimonious oxide remains unaltered when boiled with a thiosulphate, but on adding a small quantity of hydrochloric acid, the red sulphide is slowly formed; only a small portion, however, of the oxide can be converted into sulphide by this method, notwithstanding the amount of acid added.

Antimony oxychloride readily gives the cinnabar-red precipitate on boiling with a thiosulphate solution, even without the addition of acid.

J. J. S.

**Action of Alkali Sulphides on Auric Sulphide.** By UBALDO ANTONY and ADOLFO LUCCHESI (*Gazzetta*, 1896, **26**, ii, 350—353).—Auric sulphide, $Au_2S_3$, dissolves in sodium monosulphide solution at 3—4° giving an odourless, reddish liquid which, however, rapidly becomes yellow and acquires the characteristic odour of the polysulphides. On pouring the odourless solution into absolute alcohol, an oily heavy mass is deposited which rapidly changes into a mass of white needles; the latter consist of *sodium sulphaurite* $Na_3AuS_2$, which is a comparatively stable substance and apparently results from the reduction of the oily sulphaurate, $Na_3AuS_3$. Sodium sulphaurite is soluble in water, and the solution gives precipitates with solutions of metallic salts; *silver sulphaurite*, $Ag_3AuS_2$ is obtained as a heavy reddish precipitate.

Similar results are obtained with potassium monosulphide.

W. J. P.

**Purple of Cassius.** By UBALDO ANTONY and ADOLFO LUCCHESI (*Gazzetta*, 1896, **26**, ii, 195—196).—On adding a smaller quantity of mercurous chloride to a solution of auric chloride than is required by

the equation $3HgCl + AuCl_3 = 3HgCl_2 + Au$, metallic gold is deposited; but if excess of mercurous chloride be added, that which remains unchanged assumes the characteristic colour of purple of Cassius; similar results are obtained with cuprous chloride. Further, if barium sulphate and mercurous chloride are suspended in water and excess of auric chloride then added, the barium sulphate takes up the gold and becomes the colour of purple of Cassius.

Since these several salts can assume the colour of purple of Cassius, it follows that the true purple of Cassius is not a compound but merely stannic acid mechanically coloured with metallic gold.

W. J. P.

**New Double Salt of Platosemidiamine.** By DAGMAR SCHOU (*Zeits. anorg. Chem.*, 1896, 13, 36—37).—A *platosemidiamine chloride carbonate* $2Pt(NH_3)_2Cl_2, Pt_2(NH_3)_4Cl_2CO_3$, is obtained by mixing a solution of potassium platinochloride in water at 40° with a mixture of ammonium hydrogen carbonate and water, and then passing carbonic anhydride through the solution until it acquires an indigo blue colour and some quantity of a blackish-blue precipitate is deposited. The solution is precipitated with alcohol, and the precipitate washed successively with water and alcohol, and dried by exposure to the air. It forms small crystals and aggregates, is sparingly soluble in water, insoluble in alcohol and ether, is gradually decomposed by cold hydrochloric acid, and, by boiling with the acid, is converted into platosemidiamine chloride. When boiled with ammonia, a small quantity remains undissolved, and the solution when saturated with hydrogen chloride and treated with potassium platinochloride gives a precipitate of Magnus's green salt. When treated with a slight excess of silver nitrate, a yellow solution of platosemidiamine nitrate is obtained.

E. C. R.

**Iridio-ammonium Compounds. VI.** By WILHELM PALMAER (*Zeits. anorg. Chem.*, 1896, 13, 211—228; see also Abstr., 1889, 352; 1891, 402 and 1165; and 1896, ii, 179).—*Iridiotetramine dichlorochloride*, $Ir(NH_3)_4Cl_3, H_2O$, has been obtained in very small quantities by the action of ammonia on iridium chloride (Abstr., 1896, ii, 179). It is extracted from the mixture thus obtained, together with ammonium chloride, by means of cold water, and is separated from the ammonium chloride by fractional crystallisation from water, or by crystallisation from 40 per cent. alcohol. It crystallises in aggregates of thin, yellowish-white needles, or, when slowly crystallised, in bright yellow prisms belonging to the monoclinic system $a:b:c = 0{\cdot}72078:1:0{\cdot}65354$; $\beta = 53° 13'$. The water of crystallisation is not entirely removed by heating at 100°. It is soluble in 15 parts of water at the ordinary temperature, and has the electric conductivity $\mu = 104{\cdot}5$ at 25° (V = 1000). When heated, it yields ammonia and ammonium chloride and a residue of metal remains. With concentrated sulphuric acid, one-third of the chlorine is evolved as hydrogen chloride. The *dichlorosulphate*, $[Ir(NH_3)_4Cl_2]_2SO_4,2H_2O$, obtained by treating the preceding compound with concentrated sulphuric acid, crystallises in thin, lustrous, bright yellow scales, gives off ammonia when heated,

and is sparingly soluble in water; the solution has a neutral reaction. The *dichlorochloroiridite*, $3Ir(NH_3)_4Cl_3 + 3IrCl_3$, is a leather-coloured precipitate, insoluble in cold water, and is attacked by concentrated sulphuric acid at 100°.

The insoluble double salt of the empirical formula $Ir(NH_3)_3Cl_3$, obtained by the action of ammonia on iridium chloride (*loc. cit.*), is partly grey and partly leather-coloured. The grey compound is attacked by concentrated sulphuric acid at 100°, the leather-coloured compound partly at 110° and partly at 100°; hence the grey compound is the double salt of aquopentamine chloride, and the leather-coloured compound the double salt of pentamine or tetramine chloride and iridium trichloride.

The reactions of the tetramine salts are described in detail. The *bromide* is precipitated in bright yellow, rhombic crystals, the *aurochloride* in orange-red, four-sided tablets, the platinochloride in bright yellow aggregates. The solutions of the tetramine salts give a violet colouration with chlorine water.

Finally, the author gives a complete *resumé* of the chemical and physical properties of the pentamine, aquopentamine, hexamine, and tetramine compounds of iridium, and compares them with the corresponding compounds of chromium, cobalt, and rhodium. E. C. R.

## Mineralogical Chemistry.

**Behaviour of Minerals when submitted to the X-Rays.** By CORNELIUS DOELTER (*Jahrb. f. Min.*, 1896, ii, 87—106).—The several minerals examined show great differences of transparency for the Röntgen rays, and no general relation between the density and transparency can be traced, but minerals with a density greater than 5 seem to be opaque. Also, no relation can be traced to the chemical composition or molecular weight, but sulphur and arsenic compounds are the most opaque, boron and aluminium compounds, as a rule, the most transparent, and in silicates the opacity increases with the amount of iron. Dimorphous minerals do not show any important differences. Crystals show only slight differences in various directions. A scale of eight degrees of transparency is given:—1 diamond, 2 corundum, 3 talc, 4 quartz, 5 rock-salt, 6 calcite, 7 cerussite, 8 realgar. Boric anhydride is even more transparent than diamond; realgar is quite opaque. For distinguishing between precious stones and their imitations, the method has a practical application. L. J. S.

**Heavy Liquids for the Separation of Minerals.** By JAN W. RETGERS (*Jahrb. f. Min.*, 1896, i, 212—221).—Penfield (Abstr., 1896, ii, 216) has mentioned that as Retgers' thallium-silver nitrate acts on mineral sulphides, it cannot be used for their separation; this is due to the oxidising action of the nitrate. Blende is energetically attacked by molten silver nitrate with evolution of nitrous fumes, and separation

of metallic silver and zinc sulphate. Thallium nitrate acts on pyrites, but, at a moderate temperature, not on blende. The acetates of thallium, silver, lead, and mercury, and various double and basic salts, as well as mixed acetates and nitrates of these heavy metals, have been examined, but the results are not very favourable, because, although the melting points are usually low, the specific gravity of the liquid is too low for use with mineral sulphides, being rarely above 3—4. Thallium-silver acetate (m. p. 75°, sp. gr. 4·8) becomes opaque owing to separation of metallic silver. Thallium-lead acetate (sp. gr. 3·6) is liquid at the ordinary temperature, and has a high index of refraction. The only ones that would be of any use are thallium acetate (m.p. 110°, sp. gr. 3·9) and thallium nitrate-acetate (m.p. 65°, sp. gr. 4·5); the former, however, owing to its low sp. gr., would be only applicable in a few cases, and the latter decomposes at temperatures above 100°. L. J. S.

**Diamondiferous Sand from Brazil.** By HENRI MOISSAN (*Compt. rend.*, 1896, **123**, 277—278).—Sand from Brazil, after removal of the siliceous constituents, was found to contain microscopic, transparent diamonds, black diamonds and graphite, together with particles of gold and platinum. It is noteworthy that in Brazil as well as at the Cape the diamonds are associated with graphite. C. H. B.

**Free Gold in Granite.** By GEORGE P. MERRILL (*Amer. J. Sci.*, 1896, [4], 1, 309—311).—A specimen labelled "gold ore, Sonora, Mexico" is an ordinary black-mica granite which, owing to weathering, is brown and friable; throughout the mass are numerous specks, rarely over 1 mm. in diam., of native gold. Pyrites and other sulphides are not present. Microscopical examination of thin sections of the rock shows the gold enclosed in the quartz and felspar as beautiful arborescent and platy forms; it therefore does not seem to be a secondary constituent which has been deposited along fissures, but to be a primary constituent which has crystallised from the original magma. Such a mode of occurrence of gold does not seem to have been before described. L. J. S.

**Nitrogen and Argon in Firedamp and in the Gas from the Rochebelle Coal Seam.** By TH. SCHLOESING, Junr. (*Compt. rend.*, 1896, **123**, 302—305).—The firedamp, collected without admixture of air and containing no oxygen, was found to contain the following proportions of nitrogen and argon.

| Mine. | Pressure of issuing firedamp in cm. of water. | Argon and nitrogen in 100 vols. firedamp. | Argon in 100 vols. firedamp. | Argon in 100 vols. nitrogen and argon. |
|---|---|---|---|---|
| Anzin | 400 | 18·1 | 0·594 | 3·28 |
| Bességes | 4 to 5 | 3·8 | 0·064 | 1·63 |
| Firminy | 16 | 0·74 | 0·012 | 1·67 |
| Liévin | 70 | 8·0 | 0·166 | 2·22 |
| Plat-de-Gier | 75 | 30·0 | 0·601 | 1·83 |
| Ronchamp | 8 | 2·8 | 0·031 | 1·09 |
| Saint-Étienne | 600 | 3·2 | 0·037 | 1·17 |

In the mines of Rochebelle there are sudden, and often violent, outbursts of gas which has the composition $CO_2$, 98·13, nitrogen

and argon 1·14, methane 0·73. 100 c.c of the gas contains 0·021 c.c. of argon and 100 c.c. of the nitrogen and argon contain 1·87 c.c of the latter.

Argon was found in all specimens of firedamp that were examined, but the proportion of nitrogen and argon in the gas varied widely. The ratio of argon to nitrogen also varied considerably, and often exceeded the ratio in atmospheric air. The most probable explanation is that the argon has been derived not directly from the atmosphere but from air dissolved in water. The possibility of some subterranean source of argon is of course not excluded. C. H. B.

**Trinidad Pitch.** By STEPHAN F. PECKHAM and LAURA A. LINTON (*Amer. J. Sci.*, 1896, [4], 1, 193—207).—The authors have made analyses of the pitch found in and near the Pitch Lake of the Island of Trinidad. The pitch found within the Lake and also that outside have very much the same composition, and in all cases the pitch is fully saturated with moisture, usually containing some 25 to 30 per cent. About 38 per cent. of the residue is sand, the rest is bitumen and fragments of vegetation and disorganised cellular tissue. The pitch which rises in the middle of the Lake has a vesicular structure. When freshly dug, its colour is brown, but if left in the sun it soon darkens, finally becoming bluish black. A large mass when placed in bright sunshine will melt to a thin pellicle upon the exposed surface and retain the larger part of the water at a temperature sufficient to remove every trace of water if it were dried in the shade. Numerous analyses are quoted. J. J. S.

**Rutile, Cassiterite and Zircon.** By HERMANN TRAUBE (*Jahrb. f. Min.*, 1896, *Beilage*, *Bd.* 10, 470—476).—By the action of potassium fluoride or of hydrogen potassium fluoride similar etch figures, indicating holohedral symmetry, were obtained on rutile, cassiterite and zircon; this similarity cannot, however, be taken to support the view that zircon is isomorphous with the other minerals.

Various analyses of rutile have shown small quantities of $Fe_2O_3$ (up to 10 per cent.), $Mn_2O_3$ and $Cr_2O_3$; and the author has artificially prepared rutile containing these oxides. By heating titanium dioxide with sodium tungstate and various oxides at a high temperature (1700°) rutile crystals were obtained which contain up to 5·4 per cent. $Fe_2O_3$, 3·01 $Mn_2O_3$ or 1.91 $Cr_2O_3$. Under the microscope, these crystals, as well as the natural crystals, do not show any inclosures, so that these oxides have been dissolved in the titanium dioxide. Cobalt and nickel oxides were not taken up in this way. A peach-coloured cassiterite containing chromium was also prepared.

The changes in colour which occur when crystals of rutile and cassiterite are heated are described, Rutile and cassiterite are acted on by potassium fluoride with the formation of $K_2TiO_6$ and $K_2SnO_6$.

L. J. S.

**Reniform Limestone from Villejuif.** By LOUIS FRANCHET (*Bull. Soc. Philomathique, Paris*, 1896, [8], 8, 10—12).—In the limestone at Villejuif are numerous reniform and globular masses very like the menilite of Menilmontant in appearance, and in fact they have

been described as such. The material is white or yellowish and very fine in grain. Sp. gr. 2·34—2·72; H. 4·5—5. Acid dissolves calcium carbonate and leaves a residue of silica. The following analyses show that the material is a siliceous limestone and not menilite, which is a variety of opal.

| $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | CaO. | SrO. | MgO. | $K_2O$. | $Na_2O$. | $CO_2$. | Total. |
|---|---|---|---|---|---|---|---|---|---|
| 36·52 | 1·31 | 0·23 | 32·19 | 0·34 | 1·69 | 0·25 | 0·38 | 27·81 | 100·72 |
| 24·16 | 1·53 | 0·21 | 38·22 | 0·42 | 2·01 | 0·23 | 0·44 | 32·84 | 100·06 |

Also traces of manganese and sulphuric acid. L. J. S.

**Northupite, Pirssonite, Gaylussite and Hanksite from Borax Lake, California.** By JULIUS H. PRATT (*Amer. J. Sci.*, 1896 [4], 2, 123—135).—The minerals here described are found associated with borax at Borax Lake, San Bernardino Co., California. Borax Lake is an alkali marsh which is usually dry, but some water collects in it during the wet seasons.

*Northupite* (compare Abstr., 1896, ii, 184).—This was found in a single boring as isolated and unmodified regular octahedra. When pure it is colourless, but owing to impurities, probably of clay and organic matter, the colour usually varies from dirty white to dark brown. It is very brittle and shows no cleavage. Sp. gr. 2·380. It is isotropic, and for sodium light $\mu = 1·5144$. The mean of two analyses is

| $CO_2$. | Cl. | $SO_3$. | MgO. | $Na_2O$. | $K_2O$. | $H_2O$. | Insol. | Total (less O for Cl). |
|---|---|---|---|---|---|---|---|---|
| 35·12 | 14·10 | 0·08 | 16·08 | 36·99 | Nil | 0·72 | 0·22 | 100·15 |

This agrees with the formula $MgCO_3,Na_2CO_3,NaCl$. Cold water acts slowly on the mineral, but hot water decomposes it rapidly with separation of magnesium carbonate. It does not decompose on exposure to air. Fusible at 1 (Kobell's scale), with evolution of carbonic anhydride, and leaving an alkaline mass. [For artificial northupite see Abstr., 1896, ii, 610].

*Pirssonite.*—This new mineral was found by C. H. Northup as isolated crystals in the same boring as the northupite. The crystals are orthorhombic and hemimorphic; $a : b : c = 0·56615 : 1 : 0·3019$. The form $e\{131\}$ is present at one end only of the crystals, this being the pyroelectric analogous pole. The mineral is colourless to white, but is often darkened by impurities; it is brittle, and does not show any cleavage. Sp .gr. 2·352; H. 3—3·5. The optical characters are given in detail; with an increase in temperature, there is a small decrease in the value of the optic axial angle. The mean of two analyses is

| $CO_2$. | CaO. | $Na_2O$. | $K_2O$. | $H_2O$. | $Al_2O_3$, &c. | $SiO_2$. | Total. |
|---|---|---|---|---|---|---|---|
| 36·07 | 23·38 | 25·70 | 0·15 | 14·73 | 0·13 | 0·29 | 100·45 |

Formula, $CaCO_3,Na_2CO_3,2H_2O$; this is like gaylussite, which has, however, $5H_2O$; the two minerals are also somewhat similar in appearance. Practically all the water is expelled below 150.° Before the blowpipe, the mineral decrepitates and fuses at 2—2·5 (Kobell's scale) to an akaline mass. The name is given after L. V. Pirsson.

*Gaylussite.*—Crystallographic and complete optical determinations have been made on very pure crystals. Sp. gr. 1·992.

*Hanksite.*—The refractive indices for sodium light are given as $\omega = 1{\cdot}4807$, $\epsilon = 1{\cdot}4614$. The usually accepted formula for this mineral is $4Na_2SO_4,Na_2CO_3$; and the potassium and chlorine shown in the two previous analyses have been considered as impurities (salt and sylvite). The author, however, finds that chlorine is present in all crystals, and that microscopical examination shows the presence of only slight impurities. The following analyses have been made on pure material; I, on tabular crystals, and II, on prismatic crystals.

| | $SO_3$. | $CO_2$. | $Na_2O$. | Cl. | K. | Insol. | Sp. gr. |
|---|---|---|---|---|---|---|---|
| I. | 45·93 | 5·65 | 43·35 | 2·21 | 2·48 | 0·19 | 2·567—2·553 |
| II. | 45·78 | 5·63 | 43·61 | 2·28 | 2·39 | 0·12 | 2·545 |

The close agreement of both these with previous analyses indicates that chlorine and potassium are not accidental. The formula is now given as $9Na_2SO_4$, $2Na_2CO_3$, KCl. Potassium and sodium do not seem to be isomorphous here, for there is just enough potassium to form potassium chloride. Few minerals contain three acid radicles, as this does.

L. J. S.

**Mysorine (Anhydrous Copper Carbonate).** By LOUIS FRANCHET (*Bull. Soc. Philomathique, Paris*, 1894, [8], **6**, 61—65).—Thomson's mysorine from Mysore, although no water is shown in his analysis, has usually been considered to be an impure malachite. In the present paper, material which probably came from the Urals is described. It is amorphous and compact, of a greenish-grey colour, and contains specks of malachite and iron oxide; fracture conchoidal; lustre slightly resinous; sp. gr. 4·398, H. 5·5. Excepting the sp. gr., these characters agree completely with those given by Thomson. The material dissolves in hydrochloric acid with effervescence and separation of sulphur and iron oxide. Analysis gave

| $CO_2$. | CuO (combined with $CO_2$). | CuO (combined with S). | S. | $Al_2O_3$. | $Fe_2O_3$. | $SiO_2$. | Loss on ignition. | Total. |
|---|---|---|---|---|---|---|---|---|
| 15·73 | 56·50 | 15·67 | 3·95 | 2·28 | 4·90 | 0·09 | 0·56 | 99·68. |

This corresponds with 72·23 per cent. of copper carbonate and 19·62 per cent. of copper sulphide. The loss on ignition probably represents the water contained in the small amount of malachite present. Beudant has stated that when malachite is gently heated it loses water and leaves a product having the characters of mysorine; the author has, however, been only able to obtain friable, black copper oxide, as the water and carbonic anhydride are expelled together. Mysorine appears to be a definite mineral species quite distinct from malachite.

L. J. S.

**A Green Mineral from Brisbane, Queensland.** By HENRY G. STOKES (*Proc. Roy. Soc. Queensland*, 1894, **10**, 11—13).—Lining joints and cavities in the schists of Adelaide Street, Brisbane, is an amorphous, compact mineral of an apple-green to dark sea-green

colour. It sometimes shows a mammillated surface, and is often streaked with white. Brittle; smooth sub-conchoidal fracture. Thin splinters are sub-translucent. Hardness, 4—5; sp. gr. 2·6. On exposure to air, it decomposes to a white powder. It is infusible, and is slightly attacked by acids. Analysis by E. Hall gave

| $P_2O_5$. | $Al_2O_3$. | V. | $H_2O$ (loss on ignition). | Total. |
|---|---|---|---|---|
| 48·25 | 29·07 | trace | 23·61 | 100·93 |

This corresponds approximately with $4Al_2O_3,5P_2O_5,18H_2O$. The colour appears to be due to vanadium. The mineral somewhat resembles turquoise. L. J. S.

**Wardite, a new hydrous basic Aluminium Phosphate.** By JOHN M. DAVISON (*Amer. J. Sci.*, 1896, [4], 2, 154—155).—Occasionally, the decomposition of the variscite from Utah (Abstr., 1894, ii, 321) has given rise to cavities in the nodules; wardite incrusts these cavities. It is light-green or bluish-green, with a vitreous lustre, and is concretionary, sometimes approaching to oolitic, in structure. Sp. gr. 2·77; H. about 5, being a little harder than variscite. Analysis gave

| $P_2O_5$. | FeO. | CuO. | MgO. | $Na_2O$. | $K_2O$. | $H_2O$. | $Al_2O_3$ [diff.]. |
|---|---|---|---|---|---|---|---|
| 34·46 | 0·76 | 0·04 | 2·40 | 5·98 | 0·24 | 17·87 | [38·25] |

Formula: $P_2O_5$, $2Al_2O_3$, $4H_2O = Al_2(OH)_3PO_4 + \frac{1}{2}H_2O$; or, perhaps, $AlNaPO_4$, $Al(OH)_3 + \frac{1}{2}H_2O$. The following series is made out.

| | |
|---|---|
| Peganite ..................... | $Al_2(OH)_3PO_4 + 1\frac{1}{2}H_2O$ |
| Turquoise ..................... | $Al_2(OH)_3PO_4 + 1\ H_2O$ |
| Wardite ..................... | $Al_2(OH)_3PO_4 + \frac{1}{2}H_2O$ |

Before the blowpipe, the mineral swells up and turns white. It is only partially decomposed by acids; hot aqua regia leaves 20 per cent. undissolved, this is, however, soluble after being ignited. When first ignited, about 11 per cent. is insoluble in acids. The name is given after H. A. Ward.

Analyses of the *variscite* agree with that of Packard (Abstr., 1894, ii, 321), but, contrary to his statement, this mineral is completely soluble in aqua regia and in sulphuric acid. At 100—130° it gives off 22·22 per cent. of water, and on ignition 0·50 per cent. more. A pure white variscite from this locality is mentioned, the usual colour being green. L. J. S.

**Crocoite from Tasmania.** By CHARLES PALACHE (*Amer. J. Sci.*, 1896, [4], 1, 389—390).—A crystallographic description is given of crocoite from the silver-bearing lead deposits of Adelaide mine on Mount Dundas, west coast of Tasmania. The light hyacinth-red crystals rest on a matrix of lamellar limonite; they are prismatic in habit, and are translucent with adamantine lustre (compare Abstr., 1896, ii, 657). L. J. S.

**Constitution of the Silicates.** By FRANK W. CLARKE (*Bull. U.S. Geol. Survey*, 1895, No. 125, 1—109. Compare Abstr., 1888, 659; 1891, 529).—The author here summarises his views on the constitution of the

naturally occurring silicates and their relations to one another, and in a complete and connected account of the whole series discusses each species in detail. Even when the empirical formulæ have been definitely determined, which, owing to impure material, isomorphous replacements, and defective analyses, has not yet been done in very many cases, there is no method of determining molecular weights, so that attempts to arrive at the constitution of the silicates must be more or less speculative. Simplicity of structure is, however, to be inferred from the occurrence of only a limited number of definite minerals, which are usually exceedingly stable salts and have been formed under special conditions. Of importance in showing the relation in structure of one mineral to others is the study of its alteration products, as shown by pseudomorphs and by such experiments as those of Lemberg, Friedel and others.

All the silicates are considered as salts of one or other of the following silicic acids :—Ortho-, $H_4SiO_4$ ; meta-, $H_2SiO_3$ ; diortho-, $H_6Si_2O_7$ ; dimeta-, $H_2Si_2O_5$ ; tri-, $H_4Si_3O_8$. Besides normal salts, there are also double salts, and basic and acid salts, and it is often impossible to distinguish between these ; for example, $Al_2SiO_5$ may be expressed as a basic metasilicate by three different structural formulæ, or as an orthosilicate by two. A large number of minerals may be most easily interpreted as orthosilicates, and, most of these being salts of aluminium, they can be considered as substitution derivatives of the normal salt, $Al_4(SiO_4)_3$, which is taken to be a fundamental molecule in this theory of the silicates. This salt, which is possibly represented by the mineral xenolite, can be written structurally in several different ways ; the one here adopted is $Al⋮[(SiO_4)⋮Al]_3$. The following groups are then made out, and, under the various heads, the constitution and relations of all known silicates which can be referred to mineral species are minutely discussed.

*Orthosilicates of aluminium.*—I. The nephelite type.—Here one atom of aluminium is replaced by $R'_3$ ; for example, nephelite, $Al_3(SiO_4)_3Na_3$ ; muscovite, $Al_3(SiO_4)_3KH_2$ ; topaz, $Al_3(SiO_4)_3(AlF_2)_3$ ; andalusite, $Al_3(SiO_4)_3(AlO)_3$. This brings out the relation between topaz and andalusite, and their alteration to muscovite.

II. The garnet-biotite type.—Here the general formula is $Al_2(SiO_4)_3R'_6$. Of the three subtypes, the first includes natrolite, $Al_2(SiO_4)_3Na_2H_4$ ; the second biotite, $Al_2(SiO_4)_3Mg_2HK$ ; and the third the garnets, $R'''_2(SiO_4)_3R''_3$, and the epidote group, $R'''_2(SiO_4)_3R''_2(R'''OH)$. The relations between garnet, epidote and idocrase are discussed. Sodalite, $Al_2(SiO_4)_3Na_4(AlCl)$, and cancrinite, $Al_2(SiO_4)_3Na_4H(AlCO_3)$, are placed in this group.

III. The felspars and scapolites.—There is a parallelism between these two series, and both yield muscovite and kaolin as alteration products. The end members of the series are expressed as : albite, $Al(Si_3O_8)_3Na_3Al_2$ ; anorthite, $[Al(SiO_4)_3Al_2Ca]_2Ca$ ; marialite, $Al(Si_3O_8)_3Na_4Al(AlCl)$ ; meionite, $[Al(SiO_4)_3Al_2Ca]_2Ca_2O$. Kaolin is given as $OH\cdot Al(SiO_4)_2AlH_3$. Leucite is related to the feslpars and garnets, and is written as a pseudometasilicate, $Al(Si_3O_8)_2(SiO_4)_2K_4Al_3$.

IV. The normal zeolites.—These are related to nephelite and the felspars, and may be called felspathic zeolites (Abstr., 1894, ii, 459).

V. The micas and chlorites.—(Abstr., 1890, 460; 1892, 125, 794; 1893, ii, 78; 1896, ii, 37.)

VI. The tourmaline group.—Four types of tourmaline are given, and are written as two $Al(SiO_4)_3R'''_2(Al\cdot BO_2)$ groups connected by $Al(BO_3)NaH$, where R''' is Al, $R'_3$ or MgH; this formula explains the alteration of tourmaline to mica. Axinite and some other borosilicates are considered here.

VII. Miscellaneous species.—For staurolite is suggested

$$[Al(SiO_4)_3(AlO)_6Fe]_2Fe.$$

*Orthosilicates of the Dyad Bases.*—It is here necessary in most cases to assume polymerisation; for example, the members of the humite group, as recently shown by Penfield and Howe, are derivatives of the salts $Mg_8(SiO_4)_4$, $Mg_6(SiO_4)_3$, and $Mg_4(SiO_4)_2$. And owing to the existence of trimerite, $Be_3Mn_2Ca(SiO_4)_3$, phenakite is written with the triple formula $Be_6(SiO_4)_3$. The constitution of serpentine is discussed, and is expressed as $H_3(MgOH)Mg_2(SiO_4)_2$. The structural formulæ of these are written as rings or series of rings, others are written as open chains, for example, dioptase, $Cu_3(SiO_4)_4H_8Cu$.

*Orthosilicates of Tetrad Bases.*—To zircon is given the polymeric expression $Zr(SiO_4)_4Zr_3$, and from this other zirconium silicates are derived. Auerbachite is $Zr_4(Si_3O_8)(SiO_4)_3$; and eudialyte and eucolite are mixtures of tri- and orthosilicates forming a group like the felspars. Thorium and titanium silicates find a place here.

*Diorthosilicates.*—Although ethereal salts of $H_6Si_2O_7$ are known, the metallic salts are uncertain. The typical member of the group is barysilite, $Pb_3Si_2O_7$, and other lead silicates belong here. Apophyllite is given as $Ca_2(Si_2O_7)_3H_{12}(CaOH)_2$, and to it okenite and gyrolite are related. Cordierite seems to be the only aluminium salt.

*Meta- and Dimetasilicates.*—These are not easy to interpret, and in the case of the pyroxenes and amphiboles the analyses show variations from the metasilicate ratio. Wollastonite and pectolite are given as $Ca_2(SiO_3)_3Ca$ and $Ca_2(SiO_3)_3NaH$ respectively, as being chemically dissimilar from the normal pyroxenes. The fact that spodumene splits up on alteration into eucryptite and albite suggests that it is a mixed ortho- and tri-salt, to be written as $Al_6(Si_3O_8)_3(SiO_4)_3Li_6$; by analogy the other pyroxenes are also written as pseudometasilicates, $R''_8(Si_3O_8)_2(SiO_4)_2$; and Tschermak's aluminous constituent of augite is taken six times as $Al_6(SiO_4)_3(SiO_4)_3(AlO_2Mg)_6$. As the amphiboles have a less specific gravity than the pyroxenes, they may be supposed to have smaller molecules (this is opposed to the usually accepted formulæ $CaMgSi_2O_8$ and $CaMg_3Si_4O_{12}$ of diopside and tremolite respectively), and, considering them as pseudometasilicates with the bases replaceable by fourths, the formula may be written as $R''_4(SiO_4)(Si_3O_8)$; glaucophane is $Mg_2Na_2(AlO)_2(Si_3O_8)_2$. The pyroxenes are then bipolymerides of the amphiboles, and the character of the structure is the same for both groups.

Petalite, $AlLi(Si_2O_5)_2$, and milarite, $HKCa_2Al_2(Si_2O_5)_6$, are dimetasilicates, and so are mordenite and ptilolite (Abstr., 1893, ii, 77).

L. J. S.

**Microcline from the Spessart.** By E. PHILIPPI (*Ber. Senckenb. Ges. Frankfurt*, 1896, 125—133).—In the gneiss of the Spessart Mountains near Damm and Aschaffenburg are pegmatite veins containing pale flesh-red felspar. The cleavage angle, 001 : 010, of this felspar varies from 90° 1′ to 90° 11′; macroscopically, no albite lamellæ are seen. As shown by micro-chemical reactions, the small amount of soda varies in quantity, and, for the following analysis, a specimen containing apparently the average amount was selected.

| $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | CaO | MgO. | $K_2O$. | $Na_2O$. | Loss on ignition. | Total. |
|---|---|---|---|---|---|---|---|---|
| 63·84 | 19·74 | 0·03 | 0·21 | 0·06 | 13·42 | 1·82 | 0·39 | 99·51. |

Sp. gr. 2·562. The amount of calcium corresponds with 1·10 per cent. of anorthite, and the sodium with 15·75 per cent. of albite. After deducting this plagioclase material, and calculating the remaining silica, alumina, and potash to 100, the composition of the potash felspar is $SiO_2$ 63·84, $Al_2O_3$ 19·85, $K_2O$ 16·31; here there is an excess of 1·42 per cent. of alumina over the theoretical amount, which indicates commencing alteration, a fact also shown by the microscopical examination.

The angle of optical extinction on *b*(010) is 5—7°, as in orthoclase; on *c*(001), it varies from 2° to 16°. The mineral is a microcline-perthite, with albite lamellæ usually in one direction only; the microscopical characters of these lamellæ are described in detail.

L. J. S.

**Rocks and Asbestos from Corsica.** By M. OELS (*Jahrb. f. Min.*, 1896, i, Ref., 46; from *Inaug.-Diss. Erlangen*, 1894).—Actinolite-asbestos from Luri and Morosaglia, Corsica, gave the following results on analysis.

| $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MgO. | CaO. | $H_2O$. | Total. | Sp. gr. |
|---|---|---|---|---|---|---|---|---|
| 55·65 | 1·73 | 2·45 | 0·13 | 23·56 | 14·64 | 0·98 | 99·14 | 2·99 |
| 56·84 | 2·64 | 1·05 | 0·36 | 24·05 | 14·18 | 1·89 | 101·01 | 3·09 |

Several analyses of serpentine, as well as of some other rocks, are given.

L. J. S.

**Pyrophyllite from the Urals.** By FRANZ LOEWINSON-LESSING (*Verh. russ.-k. min. Ges.*, 1895, [2], 33, 283—287).—The pyrophyllite occurring in radial aggregates at Pychminsk, near Beresovsk, is shown to consist of a mechanical mixture of two minerals which may be separated by means of Thoulet's solution. The heavier portion gave analysis I, this corresponding with $3H_2O,3Al_2O_3,11SiO_2$, and so being near to the formula usually given for pyrophyllite, namely,

$$H_2O,Al_2O_3,4SiO_2;$$

the lighter portion gave analysis II., this corresponding with $3RO,8H_2O,4Al_2O_3,9SiO_2$, and is therefore distinct from pyrophyllite,

which it closely resembles in appearance; the name *pseudopyrophyllite* is given to this lighter mineral.

| | $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MgO. | CaO. | Loss on ignition. | Total. | Sp. gr. |
|---|---|---|---|---|---|---|---|---|---|
| I. | 64·94 | 29·22 | — | — | 0·16 | 0·67 | 5·90 | 100·89 | 2·782 |
| II. | 43·68 | 32·60 | 3·13 | 0·30 | 9·08 | 0·59 | 11·52 | 100·90 | 2·687 |

Hermann's analysis of the Pychminsk mineral agrees fairly closely with a mixture of three parts of pyrophyllite and one of pseudopyrophyllite. The pseudopyrophyllite is harder, and greener in colour than the pyrophyllite; both are orthorhombic, with a very perfect basal cleavage; the acute optical bisectrix is perpendicular to the cleavage, and the dispersion of the axes is feeble with $\rho > v$. Pseudopyrophyllite differs from pyrophyllite in having a larger optic axial angle, and in being optically positive. The microscopical examination points to a variability in the composition of pseudopyrophyllite.

L. J. S.

**A Crystal of Labradorite from Gabbro.** By N. H. Winchell (*Bull. Mus. Hist. Nat.* (*Paris*), 1896, 160—161).—Blocks of gabbro from Bearev Bay, Minnesota (N.E. shore of Lake Superior), contain large crystals of labradorite; one of these crystals is described. Optical extinction angle on *b* (010) 25—27°, on *c* (001) 7—11°; sp. gr. 2·72. Analysis gave

| $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | CaO. | MgO. | $K_2O$. | $Na_2O$. | Total. |
|---|---|---|---|---|---|---|---|---|
| 50·75 | 32·80 | 0·22 | — | 13·69 | 0·04 | 0·12 | 2·60 | 100·22. |

This is between $Ab_1\ An_2$ and $Ab_1\ An_3$, and corresponds with labradorite-bytownite.

L. J. S.

**Alteration of Glauconite.** By K. D. Glinka (*Annuaire Géol. Min. de la Russie*, 1896, 1, Mem. 1—3).—Gümbel has stated that glauconite alters to limonite, and Koudriavtseff gives silica as an alteration product of this mineral. It is pointed out that mineral waters from glauconite rocks contain iron and potassium, and the hydrated iron oxides which cement these rocks have probably been derived from the glauconite. Analyses of the altered mineral show that with a decrease in the iron and potassium there is an increase in the aluminium, the end product then being a ferruginous clay. Reasons are given for doubting Koudriavtseff's conclusion that silica is an end product.

L. J. S.

**Artificial Production of Rocks by Fusion in the Presence of Various Agents.** By Cornelius Doelter (*Jahrb. f. Min.*, 1896, i, 211—212). K. Schmutz, under the direction of the author, has fused natural rocks in the presence of various agents; the fused products consist of a glassy base containing the minerals mentioned below. When eclogite was fused with calcium and sodium fluorides, the resulting glass contained meionite and plagioclase. Leucitite with calcium chloride gave orthoclase; with sodium fluoride and potassium silicofluoride, it gave scapolite, mica and magnetite; and with sodium chloride the same rock gave augite, scapolite and magnetite. Granite

with sodium chloride and potassium tungstate gave plagioclase, augite, and tridymite; in the presence of other agents, olivine, augite or scapolite accompanied the plagioclase. Nephelite-basalt with calcium fluoride, sodium chloride and boric acid gave magnetite, anorthite and augite. A chlorite-schist containing pyrites when fused with sodium and aluminium chlorides gave oligoclase, mica, pyrites, and haüyne. L. J. S.

**Analcite Diabase from California.** By HAROLD W. FAIRBANKS. (*Jahrb. f. Min.*, 1896, ii, Ref., 89—90; from *Bull. Dept. Geol. Univ. California*, 1895, 1, 273—300).—In San Luis, Obispo Co., California, are three isolated occurrences of analcite-diabase in large dykes; these rocks are interesting on account of their relations to teschenite and theralite. The rock of the most important of these, the Cuyamas dyke, is much decomposed, and contains, in order of formation, magnetite, olivine, a plagioclase near labradorite, augite, and analcite; the structure is granular. Intersecting the main dyke are numerous smaller dykes, in which the rock is fresh and contains the same minerals as before, with the exception of olivine; here the structure is panidiomorphic. The analcite occurs under four different conditions: (1) lining cavities, (2) filling angular spaces between the felspar crystals, (3) replacing felspars, (4) in one of the dykes in the form of hexagonal or rounded grains partly enclosed within the felspars; it is considered to be an alteration product of nephelite. Secondary felspar and prehnite replace analcite. Analysis by V. Lenher of the rock from one of the secondary dykes gave—

| $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | CaO. | MgO. | $K_2O$. | $Na_2O$. | $H_2O$. | Cl. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|
| 50·55 | 20·48 | 2·66 | 4·02 | 7·30 | 4·24 | 2·27 | 8·37 | 0·44 | trace | 100·33 |

L. J. S.

**Comendite, a new Rhyolite.** By S. BERTOLIO (*Jahrb. f. Min.*, 1896, ii, Ref., 76—77; from *Rend. Accad. Lincei*, 1895 [5], 4, Sem. 2, 48—50).—The island of S. Pietro, off the west coast of Sardinia, consists of very acid volcanic rocks; these are liparites rich in alkalis, and containing much quartz and chalcedony. Basic minerals are subordinate; biotite and hornblende occur in some of the rocks, but more usual is a pyroxene resembling ægyrite, which shows the pleochroism $\mathfrak{c}$ bright yellow, $\mathfrak{b}$ green-yellow, $\mathfrak{a}$ leaf-green. Liparites with an alkali pyroxene form a new group, to which the name *comendite*, from the locality Comende, is given. The rock also contains an amphibole resembling arfvedsonite, with pleochroism $\mathfrak{c}$ brown, $\mathfrak{a}$ greenish-yellow. In a previous paper (*Boll. Com. Geol. Ital.*, 1894, 25, 407), the author gives the following analysis of this rock.

| $SiO_2$. | $Al_2O_3,Fe_2O_3$. | CaO. | MgO. | $K_2O$. | $Na_2O$. | Total. |
|---|---|---|---|---|---|---|
| 80·3 | 9·2 | trace | 0·6 | 3·9 | 5·5 | 99·5. |

L. J. S.

**Green Slate from Llanberis.** By JOHN H. COSTE (*Ber.*, 1896, 29, 2450—2451).—Green slate from the Dinornwig quarry near Llanberis gave the following results on analysis: the composition is

similar to that of a clayey soil. The portion soluble in strong hydrochloric acid gave I, and the insoluble portion II.

| | $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | CaO. | MgO. | Not det. |
|---|---|---|---|---|---|---|---|
| I. | — | 4·79 | 1·52 | 3·96 | 0·22 | 2·14 | — |
| II. | 77·37 | 18·68 | 1·60 | — | trace | — | 2·35 |

| | $Na_2O, K_2O$. | $P_2O_5$. | Insol. | Loss on ignition. | Total. |
|---|---|---|---|---|---|
| I. | 0·13 | 0·41 | 85·06 | 1·34 | 99·57 |

The presence of phosphoric acid is noteworthy. Seminormal hydrochloric acid acts appreciably on the rock, and extracts 0·089 per cent. of phosphoric acid. Sp. gr. of the rock = 2·818. L. J. S.

**Theralite from Costa Rica.** By JOHN E. WOLFF (*Amer. J. Sci.*, 1896, [4], 1, 271—272).—This rock forms a large intrusion in Tertiary limestone on the Atlantic slope of the Costa Rica volcanic plateau. It is a dark grey spotted rock, and shows distinct crystals of augite and biotite, and rounded areas of radiated zeolites. The microscope shows: augite, plagioclase (labradorite), sanidine, nephelite, a mineral of the sodalite group, olivine, biotite, magnetite, apatite, and analcite and other zeolites. The main differences from the Montana type are the absence of ægyrite, the distinctly basic plagioclase, and the small amount of sanidine; it is also probably poorer in alkalis. This is the nearest approach yet described to the theralite of Rosenbusch, namely, a plutonic plagioclase-nephelite rock. L. J. S.

**Altered Vesuvian Lava.** By FRANZ LOEWINSON-LESSING (*Annuaire Géol. Min. de la Russie*, 1896, 1, Section II, 10—11; from *C. R. Soc. Naturalistes St. Petersbourg*, 1895, No. 1, 15—16).—A lava stream of 1631 forms a sea-cliff at La Scala in the harbour of Resina; the long action of a warm saline solution in the form of spray has decomposed the rock to a soft, friable mass containing porphyritic crystals of augite and leucite. Analysis of this decomposed rock gave the results under I; this is compared with the average composition of Vesuvian lava II.

| | $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | CaO. | MgO. | $Na_2O$. |
|---|---|---|---|---|---|---|---|
| I. | 48·31 | 24·23 (together) | | | 9·54 | 8·24 | 4·83 |
| II. | 47·82 | 18·85 | 5·24 | 5·12 | 9·51 | 4·40 | 2·65 |

| | $K_2O$. | Loss on ignition. | Total. |
|---|---|---|---|
| I. | 2·77 | 1·73 | 99·65 |
| II. | 6·41 | — | 100·00 |

This shows that ferrous iron and potash have been replaced by magnesia and soda respectively. The material contains 1·32—1·55 per cent. of chlorine, which can be extracted by water as chlorides of sodium and magnesium. L. J. S.

**Meteoric Irons—[Rhabdite and Schreibersite].** By EMIL W. COHEN (*Jahrb. f. Min.*, 1896, ii, Ref., 42—43; from *Ann. k.k. Naturhist. Hofmuseums, Wien*, 1894, 9, 97—118).—In No. III. of his "Meteoric Iron Studies" the author gives analyses of several irons, and of the isolated rhabdite needles. It is shown that the acicular rhabdite and

the platy schreibersite have the same chemical composition, namely, $(Fe,Ni,Co)_3P$; the two occur together and only differ in habit. Goniometric measurements of rhabdite needles showed the existence of a tetragonal prism zone. The irons examined were :—I See-Läsgen, Prussia; II Bolson de Mapimi [= Coahuila], Mexico; III Sanchez Estate, Mexico; IV Hex River Mounts, S. Africa; V Schwetz, Prussia; VI Rasgata, New Granada; VII Lime Creek [=Claiborne], Alabama. The mineralogical composition of these is as follows.

| | I | II | III | IV | V | VI | VII |
|---|---|---|---|---|---|---|---|
| Nickel iron | 98·76 | 98·344 | 98·49 | 97·99 | 98·55 | 97·10 | 96·96 |
| Ni-Fe phosphides | 1·21 | 1·615 | 1·49 | 1·97 | 0·17 | 1·73 | 2·91 |
| Carbon | 0·01 | 0·011 | 0·02 | 0·02 | 0·01 | 0·07 | 0·01 |
| Chromite and silicates | 0·01 | 0·003 | | 0·02 | 0·02 | 0·03 | 0·09 |
| Daubréelite | 0·01 | 0·027 | — | | — | — | 0·03 |
| Tænite | — | — | — | — | 0·89 | 0·15 | — |
| Angular fragments | — | — | — | — | 0·36 | 0·56 | — |
| Insoluble | — | — | — | — | — | 0·36 | — |

The action of acid on the different irons of similar chemical composition is very variable, dissolution taking place in a few days, or only after an interval of months. Analysis of the portions soluble in dilute hydrochloric acid gave

| | Fe. | Ni. | Co. | P. | Cu. |
|---|---|---|---|---|---|
| I | 92·23 | 7·24 | 0·47 | 0·04 | 0·02 |
| II | 94·22 | 5·17 | 0·54 | 0·06 | 0·01 |
| III | 92·47 | 6·68 | 0·53 | 0·0469 | 0·0148 |
| VI | 92·29 | 5·50 | 0·84 | 0·15 | 0·02 |
| VII | 93·86 | 4·97 | 0·76 | 0·16 | 0·01 |

Analysis of the isolated rhabdite needles gave

| | Fe. | Ni. | Co. | P. | Cr. | S (calcd.) | Residue. | Total. |
|---|---|---|---|---|---|---|---|---|
| I | 49·06 | 35·48 | 0·45 | 13·35 | 0·48 | 0·58 | 0·63 | 100 03 |
| II | 51·60 | 30·89 | 0·70 | 14·63 | 0·78 | — | 0·96 | 99·56 |
| III | 55·01 | 28·63 | 0·60 | 15·24 | 0·43 | — | — | 100·19 |
| IV | 55·54 | 26·73 | 0·46 | 15·10 | 0·25 | 0·30 | — | 98·91 |
| VII | 47·22 | 30·16 | 0·38 | 14·16 | 0·95 | 1·16 | — | 95·57 |

With III, there is 0·28 per cent. of carbon; in IV and VII are small quantities of chromite and silicates.

Analysis of schreibersite from IV gave

| Fe. | Ni. | Co. | P. | Cr. | Chromite. | S. | Total. |
|---|---|---|---|---|---|---|---|
| 61·46 | 21·31 | 0·34 | 15·20 | 0·32 | 0·25 | 0·39 | 99·27 |

L. J. S.

**The Meteorite of Hamblen Co., Tennessee.** By GEORGE P. MERRILL (*Amer. J. Sci.*, 1896, [4], 2, 149—153).—Eakins's analyses of this meteorite (Abstr., 1894, ii, 56) showed that olivine could be present in only small quantities, for in the 37·63 per cent. of the stony portion which was soluble in hydrochloric acid only 1·34 per cent. of magnesia was present; and at the time no satisfactory conclusion was come to as to the mineral composition, beyond that the insoluble portion consisted mainly of pyroxene.

Microscopical examination by the present author shows a holocrystalline, granular ground-mass of enstatite, diallage, and anorthite, with porphyritic pyroxenes and some indeterminable material between the grains. Olivine is inconspicuous, and cannot be separated. The anorthite gave the following results on analysis.

| $SiO_2$. | $Al_2O_3$. | FeO. | CaO. | MgO. | $Na_2O$. | Total. |
|---|---|---|---|---|---|---|
| 42·02 | 37·77 | trace | 16·41 | 0·96 | not det. | 97·16 |

The enstatite was found to contain magnesium, but no calcium or aluminium. These minerals do not, however, altogether satisfy the requirements of the analysis of the soluble portion. After separating the anorthite as far as possible, some of the material is still gelatinised by acid, and, as magnesium and calcium go into solution, the presence of monticellite is suggested. When the stony portion of the meteorite is boiled with water, chlorine, sulphuric acid, calcium and iron are extracted; this suggests the presence of gypsum (derived from oldhamite) and lawrencite. The minerals probably present are then: nickel-iron, enstatite, diallage, anorthite, olivine (or monticellite), oldhamite (or secondary gypsum), lawrencite, troilite, and schreibersite.

The meteorite is to be classed as a mesosiderite; but the composition and structure are very variable, for the stony and metallic portions each in turn predominate in different parts. In the coarser portions, especially when near the metallic iron, there is a strongly marked cataclastic structure, which is well shown in the anorthite. The average sp. gr. of the fragments is 4·32.

[Eakins in a later note (*Amer. J. Sci.*, 1893, **46**, 482) had corrected some errors in his formula, and suggested that the soluble portion might consist of olivine and anorthite.] L. J. S.

**The Geologic Efficacy of Alkali Carbonate Solutions.** By EUGEN W. HILGARD (*Amer. J. Sci.*, 1896, [4], 2, 100—107. Compare Abstr., 1893, ii, 165).—The presence of alkali carbonates in mineral waters is usually explained by supposing that carbonic anhydride has extracted the alkalis from silicates; but it is better explained by the fact that alkali carbonates are formed when a solution of an alkali sulphate or chloride is treated with calcium or magnesium carbonate in the presence of carbonic anhydride. The action of alkali carbonates in soils and in hardening muds is discussed, as is their efficacy in the alteration and metamorphism of rocks, and in the formation of mineral veins. L. J. S.

**Artesian Waters of N. S. Wales.** By JOHN C. H. MINGAYE (*Australian Assoc. Adv. Sci.*, 1895, **6**, 265—277).—Nineteen analyses are given of the water from artesian bores in the western district of

New South Wales; the total solids, except in five cases, are small, and consist mainly of sodium and potassium carbonates, and sodium chloride, with less calcium and magnesium carbonates, alumina, silica, and organic matter. The value of these waters for irrigation and other purposes is discussed. Analyses of the soluble salts in two samples of soils are given. The deteriorating action on plants of alkali carbonates introduced by irrigation may be counteracted by gypsum. L. J. S.

---

## Physiological Chemistry.

---

**Oxygen Tension of Arterial Blood.** By JOHN S. HALDANE and J. LORRAIN SMITH (*J. Physiol.*, 1896, **20**, 497—520).—The aëroto-metric method of estimating the oxygen tension in blood is open to many objections that are pointed out. The value of the present method is accentuated by the fact that it is applicable to animals and men during life. The subject breathes air containing a small known amount of carbonic oxide until the percentage saturation of his hæmoglobin with that gas is constant. The final saturation with carbonic oxide of hæmoglobin solutions can be determined with quite small quantities of blood from the finger by a method previously described; it depends on the relative tensions of carbonic oxide and oxygen in the liquid, so that if the tension of carbonic oxide and the final saturation of the hæmoglobin are known, the oxygen tension can be inferred. Full details of the method of titration with carmine and a few necessary corrections are given.

It was proved that the oxygen tension of human arterial blood is 26·2 per cent. of an atmosphere or 200 mm. of mercury; as this is higher than the tension of oxygen in the alveolar air, diffusion alone will not explain the passage of oxygen from the alveolar air to the blood. Carbonic oxide is not oxidised in the body. W. D. H.

**Muscular Power and Gaseous Metabolism.** By LOUIS SCHNYDER (*Zeits. Biol.*, 1896, **33**, 289—319).—The increased discharge of carbonic anhydride that occurs during work is lessened by practice. The amount of decomposition of tissue depends on the extent of the exertion rather than of the work done. In normal individuals, the involuntary muscles are already in a state of "training," and in weakened convalescents these work with abnormal exertion even during so-called rest. W. D. H.

**The Lowest Limit of Nitrogenous Equilibrium.** By ERWIN VOIT (*Zeits. Biol.*, 1896, **33**, 333—351).—This paper is principally polemical. In it, with a few new experiments, C. Voit's original teaching is confirmed, and Munk's criticisms on this work combated.

W. D. H.

**Influence of Fat on Nitrogenous Metabolism.** By A. WICKE and HUGO WEISKE (*Zeits. physiol. Chem.*, 1896, **22**, 265—277. Compare Abstr., 1895, ii, 516; 1896, ii, 198, 535).—This is a continuation of previous work. The general conclusions are that in herbivora (sheep), gradually increasing doses of fat added to a rich proteid diet cause a smaller nitrogenous assimilation, and the output of nitrogen gets less until equilibrium is established. This has a limit which was reached in the authors' experiments when the daily dose of fat amounted to 150 to 180 grams; beyond that, nitrogenous metabolism is increased.

W. D. H.

**Preparation of Pepsin.** By CORNELIS A. PEKELHARING (*Zeits. physiol. Chem.*, 1896, **22**, 233—244).—A very powerful preparation of pepsin is obtained by dialysing artificial gastric juice against distilled water; the pepsin is precipitated, redissolved in dilute hydrochloric acid, and reprecipitated by dialysis. There is much loss of material in the process. It gives the proteid reactions and contains phosphorus (less than 1 per cent.). This may be in the pepsin or in a nucleo-proteid mixed with the pepsin, but it is not due to admixture with lecithin. By heating a solution, the phosphorus-containing substance is precipitated, and proteose goes into solution. The quantity of phosphorus in this nucleo-proteid is less (0·3 per cent.) than in the original substance; some unknown phosphorus-containing substances passing into solution. The nuclein yields alloxuric bases.

The activity of this pepsin is destroyed by alcohol, or by heating it to the temperature (60—70°) to which the precipitation just described occurs.

If commercial pepsin is digested with 0·3—0·5 per cent. hydrochloric acid, even for 5 days, it still continues to curdle milk. This is contrary to Hammarsten's statement. W. D. H.

**Bromine in the Animal Body after the Administration of Bromine Compounds.** By WERNER ROSENTHAL (*Zeits. physiol. Chem.*, 1896, **22**, 227—232).—Four dogs were fed on Paal's hydrogen-bromide-peptone added to flesh and milk. There were no toxic symptoms. After death, bromine was found in the thyroid (small quantities occur with iodine in the normal thyroid), liver, spleen, hair, pancreas, muscles and kidney in small quantities. About the same quantity is found when potassium bromide is given. W. D. H.

**Effects of the Injection of Peptone into the Circulation.** By WILLIAM H. THOMPSON (*J. Physiol*, 1896, **20**, 455—473).—In dogs, Witte's "peptone," in doses below 0·02 gram per kilo. of body weight, produces hastening of coagulation; above this dose, it causes retardation, as others have found. In doses as low as 10—15 milligrams per kilo, it causes a fall of blood pressure when the rate of injection is rapid; this is due to vascular dilatation by a direct influence on the blood vessels of the splanchnic and other areas. No indirect influence through the vaso-motor centre was observed, the

results found being practically the same even after severance of the cervical cord. W. D. H.

**Action of Carbonic Anhydride on Muscle.** By AUGUSTUS D. WALLER and Miss S. C. M. SOWTON (*Proc. Physiol. Soc.*, 1896, 16—17).—In ordinary striped muscle, stimulation in the presence of carbonic anhydride results in the staircase phenomenon. The conclusion is drawn that this phenomenon is due, as in nerve, to the evolution of the gas during contraction. With heart muscle, the effect, however, of stimulation is simply decrease in contraction and electrical response; there is no augmentation or staircase at first. Ether and chloroform act similarly. W. D. H.

**Nucleo-proteid in Muscle.** By CORNELIS A. PEKELHARING (*Zeits. physiol. Chem.*, 1896, **22**, 245—247).—Whitfield's (Abstr., 1894, ii., 358) failure to obtain nucleo-proteid from muscle is due (1) to the fact that he used water as the extracting agent; this rapidly becomes acid, and nucleo-proteids are insoluble in dilute acids; (2) gastric digestion, if the quantity of nuclein is small and the percentage of hydrochloric acid over 0·1, may not give rise to a precipitation of nuclein. In the present research, the muscles of various animals were used; the extracting agent was 0·25 per cent. solution of sodium carbonate. From the extract, which contains very little myosin, a nucleo-proteid is precipitable by acetic acid, two grams were obtained from 543 grams of flesh; it causes intravascular clotting, and contains 0·7 per cent. of phosphorus; its nuclein contains 3·5 per cent. of phosphorus and yields the alloxuric bases xanthine and guanine in small quantities. W. D. H.

**Occurrence of Inosite in the Thyroid Gland.** By R. TAMBACH. (*J. Pharm.*, 1896 [6], **4**, 119.)—This substance appears to occur in larger quantity, from 0·5 to 0·8 per cent., in the thyroid gland than in any other part of the body. M. W. T.

**Chemistry of the Thyroid.** By SIGMUND FRÄNKEL (*Wien. med. Blätter*, 1896, Nos. 13, 14, 15).—The paper gives further particulars regarding the metallic compounds of thyreo-antitoxin (Abstr., 1896, ii, 119). A second base was also separated from the proteid free extract of the gland. The gland contains a considerable quantity of inosite. The conclusion of Drechsel and Kocher, that the organ forms more than one physiologically active substance, is supported.

W. D. H.

**Chemistry of the Thyroid Gland.** By ROBERT HUTCHISON (*J. Physiol*, 1896, **20**, 474—496).—The thyroid contains two proteids, a nucleo-albumin, and the colloid matter; the former is present in small amount, and is probably derived from the epithelium. It was prepared by Halliburton's sodium chloride method. The colloid is contained in the acini. It contains a small amount of phosphorus and a considerable proportion of iodine; it yields no reducing substance on treatment with mineral acids, and no nuclein bases and is, therefore, neither a mucin, nor a nucleo-proteid. On gastric digestion, it is

readily split into a proteid and a non-proteid part; both of these, but especially the latter, contain iodine. The non-proteid part contains all the phosphorus of the original substance. The ordinary extractives are fairly abundant; but the colloid is the active physiological constituent of the gland; both parts of it are active, but the non-proteid part is the more active of the two. W. D. H.

**Chemistry of the Mucin of the Respiratory Tract.** By FRIEDRICH MÜLLER (*Centr. Physiol.*, 1896, **10**, 480—481, from *Sitz. Ges. Beförd. Naturw. Marburg*, 1896, No. 6).—The mucin of sputum was prepared by solution in alkali, and precipitation by acid and subsequently by alcohol; it is free from nuclein. After treatment with dilute sulphuric acid, it yields from 25 to 32 per cent. of a reducing substance; this is not a pentose, and the hexose prepared from it could not be identified with any known sugar; probably it may be glucosamine. W. D. H.

**The Nucleins of Pus.** By EMILE LEIDIÉ (*J. Pharm.*, 1896 [6], **4**, 150—155).—The nucleins appear to be a class of substances which differ widely amongst themselves in composition, and in the manner in which they decompose. This investigation was undertaken for the purpose of comparing the nucleins of purulent urine with those obtained from other sources. A mixture of alkali-albumins and nucleoalbumins was obtained by a method described in another paper (next abstract), and from this a nuclein. The results of the estimation of sulphur, phosphorus, and nitrogen in this substance agreed closely with those obtained by Hoppe-Seyler for a nuclein from another source. M. W. T.

**The Proteids of Purulent Urine (Pyin and Mucin).** By EMILE LEIDIÉ. (*J. Pharm.*, 1896 [6], **4**, 97—103).—The author considers that the two substances, mucin and pyin, which are usually taken as indicating the presence of pus in urine, are not originally present in the pus, but are produced by the action of alkalis on its constituents. When purulent urine, which has usually a slightly acid character, is preserved from contact with air, the leucocytes remain intact, and the liquid is found to contain neither mucin nor pyin. When the urine undergoes ammoniacal fermentation, the leucocytes quickly break up, and dissolve in the liquid. The liquid now contains both mucin and pyin, which, however, cannot be said to be derived from the broken down leucocytes, as the quantity increases with the duration of fermentation.

Pyin appears to be an alkali-albumin, and the mucin of acid purulent urine a nucleo-albumin, whilst the so-called mucin of the mucus of the bladder is probably a mixture consisting principally of a globulin. M. W. T.

**Proteids of Milk and the Methods for their Separation.** By A. SCHLOSSMANN (*Zeit. physiol. Chem.*, 1896, **22**, 197—226).—A criticism on the methods at present in use for the separation and estimation of the proteids in milk. A new method is also recommended; it consists in adding to the milk a small quantity of a saturated

solution of potassium alum at 37°. This precipitates the caseinogen in an insoluble form, and leaves the albumin and globulin unprecipitated. This is true for human, cows', asses', and pigs' milk. The globulin is precipitated from the filtrate by magnesium sulphate, and the albumin determined by difference.

In cows' milk, the numbers given are: caseinogen 3·185, globulin 0·154 and albumin 0·374 per cent. The importance of the albumin and globulin in nutrition is insisted upon. W. D. H.

**Action of Rennet.** By R. BENJAMIN. (*Virchow's Archiv*, 1896. **145**, 30—48).—This work is largely a criticism of Peter's researches (Abstr., 1895, ii, 80. Compare also Hammarsten, Abstr., 1896, i, 583, Edmunds, *ibid.*, ii, 489). The conclusions drawn are that rennet acts only on the caseinogen of milk and on no other proteid of either animal or vegetable origin; solutions of caseinogen fermentable in this way are, like milk itself, alkaline to lacmoid and acid to phenolphthaleïn; a caseinogen solution is only coagulable in the presence of soluble calcium salts. W. D. H.

**Estimation of Sulphur in Animal Tissues, and in the Hair of Animals of different Ages.** By FRANZ DÜRING. (*Zeits. physiol. Chem.*, 1896, **22**, 281—284).—Sulphur was estimated in the hair of men and animals, in hoofs, and in rabbits' flesh; the method used being a modification of Hoehnel-Glaser's. The results are very close to those of Mohr (Abstr., 1895, i, 255). The percentage of sulphur in rabbits' hairs at different ages was also investigated; the numbers lie between 3·9 and 4·6 per cent., but there is no such marked variation with age as Weiske (*Landw. Versuchs-Stat*, **36**, 81) found in birds' feathers. W. D. H.

**Physiological Action of Nitrites.** By JOHN S. HALDANE, R. H. MAKGILL and A. E. MAVROGORDATO. (*Proc. Physiol. Soc.*, 1896, 18).—Nitrites convert the hæmoglobin of the blood into a mixture of methæmoglobin and nitric-oxide-hæmoglobin. In excess, amylic nitrite causes the appearance of photomethæmoglobin. Death caused by nitrites is due simply to their action on hæmoglobin. If the oxygen in the blood plasma is simultaneously increased by administration of the gas at high pressure, this is sufficient to support life, in spite of the fact that the hæmoglobin is no longer capable of carrying oxygen. The experiments were made on mice and rabbits, and are similar in plan and results to those previously described in carbonic oxide poisoning (Abstr., 1895, ii, 407, also 1896, ii, 52). W. D. H.

**Physiological Action of the Suprarenal Capsules.** By SIGMUND FRÄNKEL (*Wien. med. Blätter*, 1896, Nos. 14, 15, 16).—The main action of an extract of the medulla of the suprarenal capsules when injected into the circulation is a rise of blood pressure. This is due to peripheral action on the small vessels, as Schäfer and Oliver (Abstr., 1895, ii, 235) showed; and as Moore (*ibid.*, 236) stated this is due to a reducing substance originally described by Vulpian. The present research is directed to an examination of this substance; this was

separated by extraction with alcohol and acetone, but not crystallised. The name *spygmogenin* is suggested for it. Its chemistry is not yet fully worked out, but its reactions point to its being a nitrogenous derivative of the ortho-dihydroxybenzene series. W. D. H.

**The Significance of Chlorides in Anæmia.** By WACLAW VON MORACZEWSKI (*Virchow's Archiv*, 1896, **145**, 458—480).—During anæmia, there is a diminution in the excretion of chlorides in the urine; the excretion increases as the patient gets better. Calcium phosphate behaves like the chlorides. The alkali phosphates and uric acid are increased in amount in the urine in the anæmic periods; this increase lessening with convalescence. An addition of calcium phosphate and sodium chloride to iron salts increases their blood-forming action. W. D. H.

**Phloridzin Diabetes.** By FREDERICK W. PAVY (*Proc. Physiol. Soc.*, 1896, 19—22).—The statement has been made that in phloridzin diabetes there is no glycohæmia. The present communication shows that if fallacies in the collection of blood, in the use of anæsthetics, and in the method employed for analysis of the blood, be avoided, there is a distinct rise in the percentage of sugar in the blood as a result of giving the drug. W. D. H.

**Action of Carbon Bisulphide on Hæmoglobin.** By NICOLAI KROMER (*Virchow's Archiv*, 1896, **145**, 188—190).—Death produced by carbon bisulphide is due to paralysis of the respiratory centre, not to any change in the blood pigment, for although this reagent causes, after the lapse of time, a partial precipitation of proteid matter, the spectrum seen is that of oxyhæmoglobin. This occurs in experiments performed in the living body and *in vitro*; there is no formation of methæmoglobin or hæmatin, as some observers have described. W. D. H.

---

## Chemistry of Vegetable Physiology and Agriculture.

**Suitability of Nodule-Bacteria of Different Origin for Various Kinds of Leguminosæ.** By FRIEDRICH NOBBE and LORENZ HILTNER (*Landw. Versuchs-Stat.*, 1896, **47**, 257—268).—Representatives of the six principal groups of the *Papilionaceæ* were grown in pots containing a mixture of sand and soil. One plant in each case was left without inoculation, the other five being inoculated with pure cultivations of nodule bacteria from (1) *Phaseolus multiflorus*, (2) *Pisum sativum*, (3) *Trifolium pratense*, (4) *Robinia pseudacacia*, (5) *Lupinus luteus*, and (6) *Ornithopus sativus* respectively. The plants selected for experiment were (1) *Phaseolus multiflorus*, (2) *Pisum sativum*, *Vicia villosa*, and *Lathyrus sylvestris*, (3) *Trifolium pratense* and *Medicago sativa*, (4) *Robinia pseudacacia*, (5) *Lupinus luteus* and *Anthyllis vulneraria*, (6) *Ornithopus sativus*. Each pot contained air-dried garden soil (1·2

kilos. containing 3·45 grams of nitrogen), pure quartz sand (6·8 kilos.), KCl (0·5 gram) and $Ca_3(PO_4)_2$ (5·0 grams). The following table shows the amount of water evaporated from the plants, indicating the relative amount of growth in each case, and also the total nitrogen in the produce.

| | Inoculated with bacteria from | | | | | |
|---|---|---|---|---|---|---|
| | Phaseolus | Pisum. | Trifolium. | Robinia. | Lupinus. | Not inoculated |
| | Evaporation (litres). | | | | | |
| 1. Phaseolus mult... | 20·17 | 8·66 | 17·46 | 12·65 | 12·89 | 11·30 |
| 2. a. Pisum sativum | 18·31 | 46·26 | 6·33 | 4·93 | 5·56 | 3·62 |
| 2. b. Vicia villosa.. | 35·46 | 44·48 | — | 6·91 | 5·76 | 3·96 |
| 2. c. Lathyrus sylv. | 3·09 | 8·10 | 4·71 | 3·70 | 5·43 | 5·65 |
| 3. a. Trifol. prat. ... | 9·01 | 6·25 | 35·83 | 7·82 | 6 58 | — |
| 4. Robinia pseudac. | 3·57 | 4·53 | 5·85 | 14·82 | 4·23 | 5·46 |
| | Total Nitrogen (milligrams). | | | | | |
| 1. Phaseolus mult... | 878 | — | — | — | — | 160 |
| 2. a. Pisum sativum | 853 | 2,791 | 125 | 105 | 142 | 56 |
| 2. b. Vicia villosa... | 2,310 | 3,444 | — | 280 | 144 | 79 |
| 2. c. Lathyrus sylv. | 49 | 384 | 68 | 62 | 78 | 81 |
| 3. a. Trifol. prat. ... | 392 | 108 | 2,136 | 123 | 123 | — |
| 4. Robinia pseudac. | 52 | 51 | 74 | 509 | 57 | 82 |

In the case of *Medicago sativa*, inoculation with Trifolium-bacteria had very little effect, whilst the other bacteria seemed to have no effect at all. The lupins failed. With regard to Anthyllis, the plants all grew much alike; only the Robinia bacteria had a slight effect. None of the serradella plants had nodules.

The results show that inoculation is only certain when bacteria from similar plants are used. Mutual availability, without essentially lessened effect, was observed only in the case of the *Viciaceæ*. Phaseolus-bacteria are effective for all the *Viciaceæ*, but the inoculation was much retarded. Pisum-bacteria were only available for the *Viciaceæ* and for *Phaseolus*, and Robinia-bacteria only for *Robinia*.

The most obvious effect of inoculation was increased vigour and development of the plants; increased flower and fruit production was also observed, especially in the case of peas and red clover. Generally, the vegetating period is prolonged by inoculation.

A period of hunger was never observed when bacteria corresponding with the plant were employed for inoculation, but when, for instance, peas and vetches were inoculated with Phaseolus-bacteria there was a long period of hunger. In sand cultures, there may be a period of hunger even when the plants are suitably inoculated, owing to the nodules not being fully developed by the time the supply of nitrogen of the seed is exhausted.

Root nodules have no essential influence on the above-ground growth as long as the soil contains sufficient nitrogen. As soon as soil nitrogen fails, leguminous plants which have no nodules are no longer able to develop. The leaves of *Leguminosæ* cannot, therefore, be the organs by means of which free nitrogen is assimilated.

N. H. J. M.

**Action of the Oxidising Ferment of Mushrooms on various Oxidisable Compounds.** By EMILE E. BOURQUELOT (*Compt. rend.*, 1896, **123**, 315—317).—The oxidising ferment of mushrooms acts on all the cresols. Orthocresol is oxidised in neutral, and also, though somewhat more slowly, in slightly alkaline solutions, with formation of a greenish-brown liquid and a dull green precipitate, soluble in ether; metacresol is oxidised under similar conditions, and yields a rose-white precipitate soluble in alcohol; paracresol is oxidised much more readily in a slightly alkaline than in a neutral solution, and the liquid becomes red and afterwards green, but the colouring matter is not soluble in ether.

Resorcinol is oxidised in neutral, but more readily in alkaline solutions, and the product is deep red with a green fluorescence.

Guaiacol is oxidised more readily in neutral or acid than in feebly alkaline solutions, and the change is very rapid; the liquid becoming orange-red, and soon depositing a red compound soluble in ether. Eugenol is oxidised under similar conditions, and a white precipitate of vanillin is formed, but no colouring matter.

Metatoluidine is oxidised very slowly in neutral solutions, but readily in presence of acetic acid, and yields a red-brown liquid and a violet precipitate; the products seem to be a wine-red substance, soluble in ether, and a violet substance insoluble in ether. Xylidine under similar conditions yields a violet-red product soluble in ether.

When aniline "for red" is dissolved in dilute acetic acid, mixed with a small quantity of an infusion of *Russula delica* and a current of air passed through the liquid, a substance of great tinctorial power, similar to magenta, is formed.

C. H. B.

**Action of the Oxidising Ferment of Mushrooms on Insoluble Phenols.** By EMILE E. BOURQUELOT (*Compt. rend.*, 1896, **123**, 423—425).—The oxidising effect of the ferment from mushrooms is exerted in solutions containing not more than 50 per cent. of ethylic or methylic alcohol, the oxidation of tyrosin, for example, taking place as readily in such solutions as in pure water. The methylic and ethylic alcohols are not affected by the ferment. These facts have been utilised to investigate the action of the ferment on various phenols insoluble in water.

Orthoxylenol yields a white precipitate, which afterwards becomes salmon colour; it is soluble in ether. Metaxylenol yields a white precipitate, which acquires a dull rose colour; it is largely soluble in ether. Paraxylenol yields a similar product which seems to be insoluble in ether.

Thymol in a slightly alkaline solution yields a white precipitate. Carvacrol in neutral solution yields a bulky white precipitate.

α-Naphthol solution becomes blue, and then violet, whilst a dull blue precipitate separates; it is partially soluble in ether, forming a mauve solution. β-Naphthol yields a white precipitate which gradually becomes yellow, and is almost completely soluble in ether. This difference might be used to distinguish between the two naphthols.

C. H. B.

**Occurrence of Titanium.** By CHARLES E. WAIT (*J. Amer. Chem. Soc.*, 1896, **18**, 402—404).—The author finds that titanium occurs in every plant ash which he has examined. Oak wood ash contains 0·31; apple and pear wood ash (mixed), 0·21; cow peas ash, 0·01; cotton-seed meal ash, 0·02 per cent. of titanium. The ash from bituminous and anthracite coal also contains titanium. The ash from Pennsylvanian anthracite coal contains as much as 2·59 per cent. J. J. S.

**Composition of Wheat Germs.** By S. FRANKFURT (*Landw. Versuchs-Stat.*, 1896, **47**, 449—470).—For qualitative examination, the germs were freed as far as possible from bran and portions of endosperm by repeated sifting, whilst the quantitative experiments were made with isolated germs picked out with the help of a lens.

In the aqueous extract employed in the examination for nitrogen compounds, albumoses, allantoin, asparagine, and a small amount of xanthine substances were found. Peptone was also present, but there is evidence that this does not exist in the germs, being produced during the digestion of the germs with warm water. Protein-dissolving ferments do not seem to be present in the free state, but in the form of a zymogen. Choline and betaine were detected, but attempts to isolate amido-acids failed. The ether extract yielded a relatively large amount of crude fat, containing lecithin and much cholesterol. With regard to carbohydrates, the germs contain cane sugar, raffinose, and small quantities of glucose, but no starch.

Wheat germs contain a ferment which vigorously inverts cane sugar at 40°, but has no effect on raffinose and very little on starch; this ferment, which is present in the free state in the germs, can be extracted by glycerol, and is precipitated by alcohol. As regards higher plants, such ferments seem only to have been hitherto detected in the pollen of *Corylus avellana* and *Pinus sylvestris* (A. von Planta, *Deut. Bienenzeitung*, 1879, No. 12).

The following quantitative results are given (per cent. in the dry substance).

| Protein-Nitrogen. | | | | | | |
|---|---|---|---|---|---|---|
| Insol. in hot water. | Soluble in hot water. | Amide nitrogen. | Crude fat. | Soluble carbohydrates. | Crude fibre. | Ash. |
| 3·46 | 2·18 | 0·80 | 13·51 | 24·34 | 1·71 | 4·82 |

The crude fat includes lecithin (1·55 per cent.) and cholesterol (0·44 per cent.). The soluble carbohydrates include 6·89 per cent. of raffinose.

The results indicate that the germs contain abundant material to develop without the aid of the endosperm. The latter would, however,

protect and ensure the development of the germs under unfavourable conditions. N. H. J. M.

**Constituents of the Seeds of Pharbitis Nil, L.** By NICOLAI KROMER (*Arch. Pharm.*, 1896, **234**, 459—480).—The author summarises his results as follows. "(1) The fatty oil of the seeds consists of the glycerides of oleic, palmitic, and acetic acids, and of a stearic acid melting at 54°; in addition, it contains a small quantity of lecithin. (2) The seeds contain a tannin, $C_{17}H_{22}O_{10}$, which turns ferric chloride solution green, and yields a yellow lead derivative containing 50·33 per cent. of lead. (3) They contain besides a carbohydrate belonging to the saccharose group; this is dextrorotatory, $[\alpha]_D = +109·53°$. I propose the name *Pharbitose* for it. (4) The resinous glucoside of the seeds is insoluble in water, and contains no nitrogen; it is lævorotatory, and has the same percentage composition as convolvulin, but is not identical with that substance. Alkali hydroxides decompose it into a glucosidic acid isomeric with convolvulinic acid, a tetrahydroxydecylic acid, and fatty acids volatile with steam, probably methylethylacetic and tiglic acids. This glucosidic acid is insoluble in ether, and is hydrolysed by mineral acids to a carbohydrate (+glucose) and a fatty acid melting at 68·5°, in all probability isomeric with convolvulinolic acid." C. F. B.

**Calculation of Proteids in Seeds from the Amount of Nitrogen.** By C. HEINRICH L. RITTHAUSEN (*Landw. Versuchs-Stat.*, 1896, **47**, 391—400).—In 1872 it was pointed out that the ordinary method of calculating the proteids in grain, &c., by multiplying the percentage of nitrogen by 6·25, gives more or less incorrect results, inasmuch as the percentage of nitrogen in pure proteids is not 16 but 16·66 to 18·4. (Ritthausen "Die Eiweisskörper d.-Getreidearten.") In order to obtain a basis for the further discussion of the subject, the author has collected the most important results respecting the composition of the proteids of seeds, and these are given in tables. With regard to the cereals and pulses, the average percentage of nitrogen in the proteids is 17·6; whilst in the oil seeds it is 18·2. In these substances, therefore, the factors would be 5·7 and 5·5 respectively. Barley, maize, buckwheat, soja and white beans are, however, exceptions. In these the factor 6·0 should be employed (the proteids containing 16·66 per cent. of nitrogen). The same factor (6·0) holds also for rape and Brassica seeds, and candle-nut.

In the published results of analyses of foods the amount of nitrogen found is very frequently omitted, the percentage × 6·25 alone being given. The percentage of nitrogen has, therefore, to be calculated before the correct factor for proteids can be applied. In the case of substances in which the proteids have been insufficiently investigated or not at all, the factor 6·25 must, of course, be retained.

N. H. J. M.

**Oxidation of Organic Matter in Soil.** By PIERRE P. DEHÉRAIN and E. DEMOUSSY (*Compt. rend.*, 1896, **123**, 278—282).—When soil is heated to 120°, carbonic anhydride is produced, and the soil when

allowed to cool and re-inoculated undergoes more rapid nitrification than the original soil, seemingly in consequence of the partial oxidation of the organic matter.

The oxidation of the organic matter of sterilised soils by air at 22° is extremely small; non-sterilised soils are, however, slowly oxidised at this temperature with production of carbonic anhydride, which, however, is less than the volume of oxygen absorbed, some of the latter being used up in oxidising hydrogen or in forming an oxidation product which remains in the soil. The rate of oxidation is higher the more readily air can permeate the soil; it is also influenced by the proportion of water, and with rich soils oxidation at 22° or 44° is at its maximum when the soil contains 17 per cent. of water, but decreases if the proportion of water falls to 10 per cent. or rises to 25 per cent. With soils less rich in humus, a somewhat higher proportion of water is necessary to retard oxidation in any marked degree, although the same minimum proportion holds good. As oxidation continues, the rate of production of carbonic anhydride becomes less and less, a result no doubt due to the fact that humus is a complex substance, some of the constituents being more oxidisable than others.

When non-sterilised soil is heated, the rate of oxidation increases slightly between 22° and 44°, becomes much more energetic at 65°, but falls off considerably at 80°, owing most probably to the destruction of the microbes. Beyond 96°, however, there is again a marked increase in the rate of oxidation. At 110° or 120° the volume of carbonic anhydride liberated is greater than the volume of oxygen absorbed, and part of the former must result from decomposition and not from oxidation. At 100°, the carbonic anhydride produced is less than the volume of oxygen absorbed, just as at 22°, water or some other oxidation product being formed. Similarly, the rate of production of carbonic anhydride at 100° falls off as the oxidation progresses.

Oxidation is so active between 40° and 60° that it is conceivable that in hot climates soils left unworked and without manure may gradually become sterile owing to the disappearance of the humus. Even at Grignon, some fields carrying various crops without addition of manure have lost half their organic matter in 10 years.

C. H. B.

**Destruction of Fat by Moulds.** By C. Heinrich L. Ritthausen and Baumann (*Landw. Versuchs-Stat.*, 1896, **47**, 389—390).—The following analyses are given of two samples of rape cake, (1) in their original state, and (2) after they had been kept for two years in a finely powdered state in stoppered bottles. The samples became covered with mould.

| | Sample I. | | | Sample II. | | |
|---|---|---|---|---|---|---|
| | Water. | Fat. | Nitrogen. | Water. | Fat. | Nitrogen. |
| In original state ......... | 12·45 | 10·53 | 5·13 | 12·31 | 8·50 | 4·86 |
| After two years (mouldy) | 21·94 | 1·98 | 5·15 | 23·42 | 1·87 | 5·12 |

The excess of water in the mouldy samples can only have been derived from the decomposed fat. Fifteen different bacteria and fungi

were isolated, and it is assumed that it is mainly to the moulds that the changes observed were due. (Compare Reitmair, Abstr., 1891, 770). N. H. J. M.

**Maize-germ Cake.** By F. J. van Pesch (*Landw. Versuchs.-Stat*, 1896, **47**, 473—475).—Maize-germ cake is a product of oil factories and is obtained in a manner similar to linseed cake. It is used as food for all kinds of cattle. The following analyses of samples of cake, stated to be "maize cake" but which were undoubtedly maize-germ cake, are given.

| | Water. | Crude protein. | Fat. | N-free extract. | Crude fibre. | Ash. |
|---|---|---|---|---|---|---|
| 1. | 18·8 | 16·2 | 3·6 | 56·7 | 2·7 | 2·0 |
| 2. | 17·2 | 17·8 | 4·0 | 59·0 | | 2·0 |
| 3. | 10·8 | 17·5 | 4·2 | 61·4 | 3·7 | 2·4 |
| 4. | 13·6 | 20·2 | 5·7 | 54·6 | 4·4 | 1·5 |
| 5. | 12·1 | 22·7 | 5·3 | 53·9 | 4·3 | 1·7 |

Maize-germs contain, according to Moser, water 11·8, proteids 12·4, fat 17·4, nitrogen-free extract 46·0, crude fibre 6·9, and ash 5·5 per cent. N. H. J. M.

## Analytical Chemistry.

**A Convenient Form of Graduated Flask.** By Wilhelm Wislicenus (*Ber.*, 1896, **29**, 2442—2445).—The author points out that Biltz's modified measuring flask (Abstr., 1896, ii, 671) is not new, he has himself for several years used a modification in which the neck of the flask is widened above the ordinary graduation mark and again constricted higher up, a second graduation mark being placed above the wider portion so that this contains exactly 100 c.c. between the two marks. In the preparation of a standard solution, 1100 c.c. are first prepared of slightly greater strength than is required. A portion of the liquid is then removed from the upper part of the flask, its strength accurately determined, and from this the amount of water to be added to 1000 c.c. is calculated. The flask is then emptied by means of a pipette down to the 1000 c.c. mark and the requisite amount of water added. A. H.

Note.—This arrangement is identical with that described by Giles (Abstr., 1894, i, 251).—Eds.

**Iodometric Estimation of Selenious and Selenic Acids.** By James F. Norris and Henry Fay (*Amer. Chem. J.*, 1896, **18**, 703—706).—Selenious acid may be estimated by mixing a measured portion of the solution containing it with ice-cold water and 10 c.c. of hydrochloric acid (sp. gr. 1·12), adding an excess of N/10 sodium thiosulphate solution, and titrating back with iodine solution. One mol. of selenious acid is equivalent to 4 mols. of sodium thiosulphate. The exact nature of the chemical change has not yet been ascertained. The

hydrochloric acid must be sufficient to liberate all the thiosulphuric acid. Before applying this method, the selenic acid is reduced by adding 25 c.c. of concentrated hydrochloric acid to a measured portion of the solution, diluting to 100 c.c. and boiling for one hour, care being taken that the volume is never less than 75 c.c. The cooled liquid is then treated as described above, except that it will probably be already sufficiently acid. A. G. B.

**Separation of Selenium from Tellurium.** By FRANK A. GOOCH and A. W. PEIRCE (*Amer. J. Sci.*, 1896 [4], 1, 181—185).—The fact that selenium bromide is volatile, whereas tellurium bromide is not, can be made use of in estimating selenium in the presence of tellurium.

With the object of testing the accuracy of the method, the author has experimented in the following way. Solutions containing known weights of selenious and tellurous anhydrides, dissolved in potash, were treated with excess of phosphoric acid in order to dissolve the precipitate which was formed at first. One gram of potassium bromide was added, and the whole introduced into a Voit flask and water added to make the volume up to 50 c.c. ; this first flask was fused to a second Voit flask containing 10 c.c. of water, and the second flask, in its turn, was fused to a Drexel bottle which had fused to its escape tube a Will and Varrentrap bulb to serve as a trap. The bottle and bulbs were filled with potassium iodide solution, and carbonic anhydride was kept slowly passing through the whole apparatus. The distillation of the products in the first flask was continued until the 50 c.c. had been reduced to 15 c.c. ; by this time all the selenium had passed over in the form of its bromide and had been collected in the second flask, a small quantity of iodine had also been liberated in the bottle owing to bromine having passed over. As a quantity of selenium bromide collected in the tube connecting the two flasks, it was necessary to drive this over into the second flask before disconnecting. The first flask was then removed, 1 gram of potassium iodide was added to the second flask, the current of carbonic anhydride was again started through the apparatus, and the mixture was boiled for 10 mins. The free iodine in the flask, Drexel bottle and trap was taken as the measure of the selenious anhydride present. The results were fairly good, the errors being 0·1—0·7 per cent. J. J. S.

**Estimation of Tellurium by Precipitation as the Iodide.** By FRANK A. GOOCH and W. C. MORGAN (*Amer. J. Sci.* [4], 2, 271—272, and *Zeits. anorg. Chem.*, 1896, 13, 169—171).—Tellurous acid may be very accurately estimated by simply adding standard solution of potassium iodide as long as it forms a precipitate. The liquid should contain at least one-fourth of its bulk of strong sulphuric acid, and when the greater part of the tellurium iodide has formed the beaker must be rotated to make the precipitate settle. More potassium iodide is then added to complete the reaction. Ten test experiments are given to show the accuracy of the process. L. DE K.

**Nitrates in Water.** By ALESSANDRI and GUASSINI (*Chem. Centr.* 1896, i, 329 ; from *Boll. Chim. farm.* 1895, 490).—A few c.c. of the

sample is evaporated to dryness, and 6 drops of a saturated solution of phenol in hydrochloric acid is at once added. Sometimes it is advisable to slightly warm the reagent. If nitrates are present, a reddish-violet coloration is obtained which on adding ammonia changes to an emerald green. L. DE K.

**Iodometric Method for the Estimation of Phosphorus in Iron.** By CHARLOTTE FAIRBANKS (*Amer. J. Sci.* [4], 2, 181—185, and *Zeits. anorg. Chem.*, 1896, 13, 117—120).—The method for titrating molybdic acid with iodine recommended by Gooch and Fairbanks (this vol., ii, 76) is also applicable to the yellow molybdic precipitate, and is, therefore, a convenient process for the estimation of phosphorus in iron. Twelve mols. of molybdic acid correspond with 1 atom of phosphorus. L. DE K.

**Estimation of Phosphates in Precipitates.** By THEODOR PFEIFFER (*Landw. Versuchs-Stat*, 1896, 47, 357—360).—Determinations of phosphoric acid in a sample of precipitate gave the following results. With strong hydrochloric acid as solvent, $P_2O_5 = 30{\cdot}96$ and $31{\cdot}10$ per cent.; with aqua regia $P_2O_5 = 33{\cdot}00$ and $32{\cdot}91$ per cent.; with a mixture of sulphuric and nitric acids $P_2O_5 = 33{\cdot}19$ per cent. It was found that the whole of the phosphoric acid in hydrochloric acid extracts is not precipitated by magnesia mixture (citrate method), and that the filtrate yielded a further amount (2·27 per cent.), when boiled with sulphuric or nitric acid. This seems to be due to the presence of pyrophosphate in the precipitate. When pure monocalcium phosphate (5 grams) was heated for a long time at 250°, dissolved in boiling hydrochloric acid, and diluted to 250 c.c., 62·64 per cent. of $P_2O_5$ was found by direct precipitation, and 68·99 per cent. after boilimg with nitric acid.

Two samples of precipitate (one of which had been slightly dried and the other not at all) were found to be free from pyrophosphate. Another sample which had been dried by heating with steam showed a distinct amount of pyrophosphate; whilst a fourth sample from England, which had been over-dried, gave a percentage of 31·10 of $P_2O_5$ before, and 32·91 after the "inversion" of the hydrochloric acid solution.

The results show that mere estimation of total phosphoric acid is misleading, especially when aqua regia is employed as the solvent.

N. H. J. M.

**The Precipitation of Phosphomolybdate in Steel Analysis.** By GEORGE AUCHY. (*J. Amer. Chem. Soc.*, 1896, 18, 170—174).—In order to ensure the complete precipitation of the phosphorus, the following process is recommended:—Two grams of steel is dissolved in 100 c.c. of nitric acid of sp. gr. 1·13, the solution is partially neutralised by adding 15 c.c. of strong ammonia previously diluted with 50 c.c. of water, and after heating to 85°, the phosphoric acid is precipitated by adding 60 c.c. of Blair and Whitfield's molybdate solution.

If it is thought desirable to precipitate from a very acid solution,

from 15—20 grams of ammonium nitrate should be first added and the liquid should be somewhat diluted. The author adds a caution as to the occasional presence of phosphoric acid in the reagents used.

L. DE K.

**Interaction of Chromic and Arsenious Anhydrides.** By PHILIP E. BROWNING (*Amer. J. Sci.*, 1896 [4], 1, 35—37).—Kessler has shown (*Pogg. Annalen*, 1855, 95, 204) that arsenious anhydride may be estimated by treating it in the presence of hydrochloric acid with an excess of a chromate of known strength. The excess of chromic acid is then determined by the addition of a ferrous salt until a drop taken from the solution gives a blue colour with a ferricyanide. Chromic acid is again added until the blue colour disappears.

The author shows that a somewhat similar method may be used for estimating chromic acid. The chromate solution is mixed with about 10 c.c. of dilute hydrochloric or sulphuric acid (1 : 4) and a carefully measured amount of N/10 arsenious acid solution is run in; care must be taken that the arsenious acid is in excess. It is not necessary to apply heat to bring about the reduction of the chromate. About 5 grams of potassium or sodium hydrogen carbonate are added to the solution, and in most cases a precipitate forms unless Rochelle salt has been previously added, N/10 iodine is then run in until the solution acquires a slightly permanent yellow colour, and the mixture is allowed to stand for about 30 minutes. The excess of iodine is destroyed by N/10 arsenious acid, starch is added, and the solution titrated with N/10 iodine.

The points to notice are that the addition of Rochelle salt gives a dark green solution and thus renders it difficult to detect the point where the iodine gives the blue colour with starch. If Rochelle salt is not added, a precipitate forms, and this contains small quantities of arsenious acid unless it is allowed to remain for some time (1—2 hours) with the excess of iodine. The method is fairly accurate, and can be carried out in the presence of ferric salts. J. J. S.

**Detection and Estimation of Borax in Butter.** By VICTOR PLANCHON and VUAFLART (*J. Pharm.*, 1896 [6], 4, 49—51).—The amount of borax present in a sample of butter can be roughly estimated by means of a colour reaction, depending on the formation of a blue compound produced by the fusion of copper oxide with borax. The ash from 20 grams of butter is fused with 0·5 grams of potassium carbonate, and a trace of copper oxide. The amount of borax present may be estimated approximately from the intensity of the blue colour produced.

M. W. T.

**Estimation of Silicon in Pig Iron.** By LIEBRICH (*Chem. Centr.*, 1896, i, 68—69; *Stahl u. Eisen*, 15, 1058).—The filter containing the silicic acid, silicon, and graphite is, without removing the iron, burnt, and the black ash is fused with dehydrated potassium hydrogen sulphate until all the carbon has disappeared. The residue, on being digested with hydrochloric acid, leaves pure silicic acid free from titanium and iron.

L. DE K.

**Detection and Estimation of Carbonic Oxide in Air.** By JOHN S. HALDANE (*J. Physiol.*, 1896, **20**, 521—522).—The method previously described for estimating the percentage of carbonic oxide in the air by means of a solution of blood requires modification in view of the fact that daylight has a marked influence on the stability of carboxy-hæmoglobin. The precautions to avoid the influence of strong light, and the necessary alterations in the table are given.

W. D. H.

**Separation and Identification of Potassium and Sodium.** By D. ALBERT KREIDER and J. E. BRECKENRIDGE (*Amer. J. Sci.*, [4], **2**, 263—268, and *Zeits. anorg. Chem.*, 1896, **13**, 161—168. Compare Abstr., 1895, ii, 444).—Potassium may be completely separated from sodium by evaporating the solution with perchloric acid and treating the residue with 97 per cent. (commercial absolute) alcohol, which soon dissolves the sodium compound, but leaves the potassium perchlorate which is quite insoluble. When dealing with a sulphate, this must first be decomposed by means of barium chloride, the excess of the latter being removed by ammonium carbonate, and the ammonium compounds expelled by ignition. The sodium is precipitated from its alcoholic solution as chloride by means of a current of hydrogen chloride, and may then be further identified. The perchloric acid must, of course, be quite free from sodium, and is, therefore, best purified by distillation under low pressure. Details for the safe preparation of the reagent are given.

L. DE K.

**Volumetric Estimation of Alkali Hydroxides containing Carbonates and of Alkali Carbonates: The Value of Phenolphthaleïn and Methyl-orange as Indicators.** By FRIEDRICH W. KÜSTER (*Zeits. anorg. Chem.*, 1896, **13**, 127—150).—The only method for the volumetric estimation of mixed solutions of alkali hydroxides and alkali carbonates which gives trustworthy results is that published by Cl. Winkler. The alkali carbonates are precipitated by barium chloride, and the solution, together with the precipitate, is titrated, using phenolphthaleïn as indicator. The total alkali is determined by titration, using methyl-orange as indicator. Methyl-orange is, contrary to the statements of previous authors, strongly coloured by carbonic acid; and in the titration of alkali containing carbonates the titration must be continued only to a known normal coloration which is defined by comparison with an equally concentrated aqueous solution of the methyl-orange saturated with carbonic anhydride. Phenolphthaleïn is also coloured by aqueous solutions of alkali hydrogen carbonates when these solutions are dilute. The coloration is weakened by the presence of sodium salts of strong acids and by carbonic anhydride, and disappears entirely in the presence of large quantities of free carbonic anhydride. This indicator cannot, therefore, be used for the direct volumetric estimation of alkali hydroxides contained in alkali carbonates. Trustworthy results are obtained only when a small quantity of carbonate is present, whereas by Winkler's method the results can be depended on irrespective of the amount of carbonate. In the presence of hydrogen alkali carbonates, the total alkali is determined with methyl-orange as indicator; the hydrogen carbonate

is estimated by adding a measured quantity of alkali hydroxide in excess, precipitating with barium chloride, and titrating, using phenolphthaleïn as indicator. The difference between the amount of alkali added and that found after precipitation gives the quantity of hydrogen carbonate present. The results obtained are too low, and the error is proportional to the amount of hydrogen carbonate present. E. C. R.

**Estimation of Cadmium as Oxide.** By PHILIP E. BROWNING and LOUIS C. JONES (*Amer. J. Sci.* [4], 2, 269—270, and *Zeit. anorg. Chem*, 1896, **13**, 110—112).—Muspratt has stated that the estimation of cadmium as oxide by igniting the carbonate gives results which are much below the truth; no better results are obtained by dissolving the carbonate in nitric acid and igniting the nitrate. The authors state that when using the Gooch asbestos filter and crucible, the carbonate may be converted into oxide without loss. Twenty-one experiments are quoted to show the trustworthiness of the process.

L. DE K.

**Estimation of Lead in Potable Waters.** By UBALDO ANTONY and T. BENELLI (*Gazzetta*, 1896, **26**, ii, 194—195).—Potable waters may contain various substances, such as silicic acid, ferric, and aluminium hydroxides, in the colloidal state and, on adding the amount of ammonium chloride necessary for the complete precipitation of the lead and mercuric sulphides in accordance with the authors' method (Abstr., 1896, ii, 549) of estimating lead in water, these hydroxides would assume the insoluble form. It is recommended that after the lead sulphate has been weighed, it should be dissolved in hot ammonium tartrate solution, and any insoluble residue weighed and allowed for.

W. J. P.

**Electrolytic Estimation of Mercury.** By EDGAR F. SMITH and DANIEL L. WALLACE (*J. Amer. Chem. Soc.*, 1896, **18**, 169—170).—The amount of mercury in cinnabar may be conveniently estimated by dissolving about 0·22 gram of the mineral in 25 c.c. of solution of sodium sulphide (sp. gr. 1·2). After diluting to 125 c.c., the liquid is electrolysed in a platinum crucible at a temperature of 70° with a current of N.D. 100 = 0·12 ampère. The precipitation of the metal is complete within 3 hours. L. DE K.

**New Method of Separating the Phosphates in the Ammonia Group.** By N. TARUGI (*Gazzetta*, 1896, **26**, ii, 256—258).—The methods in general use for separating the precipitate of metallic phosphates obtained with ammonia and ammonium chloride in qualitative analysis being inconvenient, the author has devised the following process, which gives excellent results.

The precipitate is treated with cold acetic acid, when only ferric and aluminium phosphates and many of the oxalates remain undissolved; after filtration, all the phosphoric acid and part of the oxalic acid is removed from the filtrate by adding excess of lead acetate. The lead salt is filtered off and the filtrate freed from lead by adding hydrochloric acid and then hydrogen sulphide or thioacetic acid; after boiling off the hydrogen sulphide and filtering, the filtrate is poured

drop by drop into a boiling concentrated sodium carbonate solution into which the precipitate not dissolved during the first treatment with acetic acid has been put. The only phosphate the precipitate can contain is ferric phosphate, which, however, gives no trouble in the subsequent examination of the liquid for the metals.

If the original precipitate contains no oxalates, the part insoluble in acetic acid can only contain ferric and aluminium phosphates and need only be examined for these two metals; the acetic acid solution is then treated with ammonia and ammonium chloride and examined in the ordinary way. W. J. P.

**Iodometric Estimation of Molybdic Acid.** By FRANK A. GOOCH AND CHARLOTTE FAIRBANKS (*Amer. J. Sci.*, 1896 [4], 2, 156—162).—Mauro and Danesi recommend heating the molybdate compound with hydrochloric acid and potassium iodide in a sealed tube filled with carbonic anhydride. The liberated iodine is afterwards titrated. Friedheim and Euler prefer submitting the mixture to distillation and titrating the iodine in the distillate.

The authors have found that the molybdic acid is best estimated by acting on the residue with iodine in the presence of an alkali. A quantity of molybdic acid, in the form of an alkali salt, not exceeding 0·3 gram is mixed up with 20 c.c. of water, 20 c.c. of hydrochloric acid (sp. gr. 1·20) and 0·5 gram of potassium iodide, and after introducing the liquid into a narrow flask it is rapidly boiled down to 25 c.c. but not further. The residue, after adding 1 gram of tartaric acid, is nearly neutralised with aqueous soda, and then mixed with a slight excess of sodium hydrogen carbonate. A definite quantity of iodine solution is now at once added, and the corked bottle is set aside for 2 hours. The excess of iodine is titrated by means of arsenious oxide. One atom of iodine corresponds with 1 mol. of molybdic acid. L. DE K.

**Application of the Blue Oxide of Molybdenum in Volumetric Analysis.** By ATTILIO PURGOTTI (*Gazzetta*, 1896, ii, 197—220).—The blue oxide of molybdenum, $Mo_3O_8$, is readily oxidised by such substances as permanganates, chromates, hypochlorites, chlorine, peroxides, ferric salts, and platinic and auric chlorides, and since the oxidation of the whole of the oxide is rendered evident by the disappearance of the characteristic blue colour, it may be used for the volumetric estimation of oxidising agents. The reduction of molybdic anhydride occurs in two stages in accordance with the equations $5MoO_3 + 16H = Mo_5O_7 + 8H_2O$ and $Mo_5O_7 + 19MoO_3 = 8Mo_3O_8$, so that if a solution containing $5MoO_3$ be completely reduced to the brown oxide, $Mo_5O_7$, and then added to a solution containing $19MoO_3$, this will contain only the blue oxide. The standard solution of the blue oxide is made by reducing 1·1 gram of ammonium molybdate, $(NH_4)_6Mo_7O_{24}, 4H_2O$, dissolved in 30 c.c. of water and 5 c.c. of pure sulphuric acid with 4—5 grams of zinc dust; after filtering the brown solution, it is made up to 200 c.c. and added to a solution of 4·2 grams of ammonium molybdate and 2 c.c. of pure sulphuric acid in 800 c.c. of water. The solution is then boiled until blue, and on cooling is ready for use; it is approximately N/50, and cannot be made N/10 because of the

sparing solubility of the oxide. The standardising is performed by diluting 10 c.c. of N/100 potassium dichromate to 30 c.c., adding 3 c.c. of 1 : 3 pure sulphuric acid, and running the molybdenum solution into the hot solution until a persistent blue colour is observed; the solution does not change in strength if preserved in well-closed full vessels.

For the indirect estimation of substances such as cupric salts which are not reduced by blue molybdenum oxide, the author does not use standard ferrous sulphate solution but prefers to reduce them with alkaline chromium hydroxide solution and subsequently estimates the chromate formed by titration with molybdenum solution. 10 c.c, of 16 per cent. chrome alum solution is mixed with 30 c.c. of 30 per cent. caustic potash giving an alkaline solution of about 0·32 gram of chromium hydroxide; this is boiled for about 15 minutes with 10 c.c. of a cupric salt containing about 0·15 gram of copper. The excess of chromium hydroxide is thus rendered insoluble, and potassium chromate remains in solution; the latter is then estimated by filtering the solution, making up to a standard volume and titrating an aliquot part with molybdenum solution after acidification with sulphuric acid.

The titration of hot permanganate or hot dilute ferric solutions with molybdenum solution gives excellent results. Good results are obtained in the estimation of lead by precipitating it as chromate and filtering, washing and dissolving the precipitate in caustic potash; the solution is then acidified with sulphuric acid and titrated with molybdenum solution. Lead solutions may also be boiled with calcium hypochlorite in feebly acid solutions and the precipitated lead peroxide filtered, washed and boiled with the alkaline chromium hydroxide as described above. After separating the insoluble chromium hydroxide, the filtrate is acidified with sulphuric acid and titrated with molybdenum solution.

Silver chloride or sulphate may be estimated by boiling with alkaline chromium hydroxide, when metallic silver is formed; the chromate produced is then estimated with molybdenum solution. The results obtained with silver nitrate solution are rather too high owing to the slight action of the nitric acid on the molybdenum solution. Both mercuric and mercurous salts are reduced to metallic mercury by alkaline chromium hydroxide solution, and may be estimated indirectly by titrating the chromate with molybdenum solution. Nickel and cobalt salts are converted into the sesquioxides by heating with calcium hypochlorite or sodium hypobromite solution and may then be estimated in the same way as lead peroxide. Good test results were obtained with all the methods described above; the presence of nitric acid is, however, to be avoided in titration with molybdenum solution.

W. J. P.

**Reactions of Tungsten.** By E. Defacqz (*Compt. rend.*, 1896, **123**, 308—310).—When a tungsten compound is converted into tungstic acid, heated with four or five times its weight of potassium hydrogen sulphate and a few drops of sulphuric acid, and then mixed with sufficient concentrated sulphuric acid to prevent solidification on cooling, the liquid obtained gives colour reactions with a large number

of organic compounds. The best results are obtained with phenols and alkaloids, and the most important of these reactions are as follows :—*phenol*, very intense deep red; *quinol*, very intense amethyst-violet; *catechol*, violet black; α- or *β-naphthol*, violet-blue; *salicylic acid*, very intense deep red; *veratrine*, intense sienna colour. Many of the alkaloids give no coloration, and of the various compounds used phenol and quinol are the most valuable for analytical purposes, the reaction with them being much more sensitive than the well-known production of a blue coloration by the action of zinc or some similar metal. As a rule, the colorations disappear on adding water. C. H. B.

**Reduction of Vanadic Acid by Hydriodic and Hydrobromic Acids, and its Titration in Alkaline Solution with Iodine** By PHILIP E. BROWNING (*Amer. J. Sci.*, [4], 2, 185—188, and *Zeits. anorg. Chem.*, 1896, 13, 113—116).—The solution containing the vanadate is boiled in an Erlenmeyer beaker with potassium iodide or bromide and a regulated amount of sulphuric acid, until no more iodine or bromine is liberated. After cooling, the residual liquid is nearly neutralised with aqueous potash, a small quantity of tartaric acid is added, and the neutralisation completed with an excess of potassium hydrogen carbonate. Excess of standard iodine is then added, and after remaining for half an hour in a closed bottle, the free iodine left is estimated by means of a solution of arsenious oxide.

One mol. of iodine represents 1 mol. of vanadic acid. L. DE K.

**Estimation of Bismuth.** By WILHELM MUTHMANN AND F. MAWROW (*Zeits. anorg. Chem.*, 1896, 13, 209—210).—The faintly acid solution of the bismuth salt is treated with an excess of hypophosphorous acid, and warmed on the water bath until the supernatant liquid is clear and a further addition of hot hypophosphorous acid does not cause any coloration. The reddish-grey precipitate of metal thus obtained is easily collected; after being washed with hot water, and with absolute alcohol, it is dried at 105°, and weighed either on a tared filtered paper or in a Gooch's crucible. The results are very accurate. The method is especially useful for the separation of bismuth from those metals which are not precipitated by hypophosphorous acid, such as zinc and cadmium.

E. C. R.

**Platinum Amalgam and its Application in Analysis.** By N. TARUGI (*Gazzetta*, 1896, 26, i, 425—431).—Magnesium precipitates the whole of the mercury and platinum, from a solution containing both mercuric and platinic chlorides, as a black precipitate in which, even when it contains only 1 per cent. of platinum, no metallic mercury can be detected under the microscope. Further, the precipitate is always readily soluble in concentrated nitric acid, even if it only contains 1 per cent. of mercury, but if precipitated mercury and platinum be mixed, nitric acid dissolves mercury alone from the mixture; the solubility of the amalgam is therefore not due to the retention of chlorine by the precipitated metals.

The author proposes to apply these facts to the qualitative analysis of solutions which may contain gold, mercury, and platinum. The gold is first precipitated by oxalic acid, and, after separating it, magnesium is added to the filtrate; a grey precipitate can only be mercury, a black precipitate insoluble in nitric acid is platinum, whilst a black precipitate soluble in nitric acid shows that both platinum and mercury are present. W. J. P.

Separation of Palladium from Platinum. By PAUL COHN and FRANZ FLEISSNER (*Monatsh.*, 1896, **17**, 361—364).—The solution of the two metals in aqua regia is repeatedly evaporated with water in order to eliminate nitric acid, and again with about 10 c.c. of a 10 per cent. solution of ammonium chloride. The residue is then warmed with a few drops of water, and covered with a 30 per cent. solution of ammonium chloride, when ammonium platinochloride is gradually precipitated, this is separated by filtration, and washed, first with a solution of ammonium chloride and then with alcohol, and is finally transferred to a platinum crucible and heated to redness. The palladium chloride present in the filtrate is mixed with fairly strong nitric acid, and the whole evaporated on the water bath, when a beautifully crystalline red precipitate is formed; this is collected, and washed with a strong solution of ammonium chloride to which a few drops of nitric acid have been added. The precipitate consists of *ammonium palladiochloride*, $Pd(NH_4)_2Cl_6$; if insufficient nitric acid has been used, a brown basic salt is obtained instead.

The red ammonium palladiochloride is sparingly soluble in cold water, and is decomposed by warm water, with production of ammonium palladious chloride, $(NH_4)_2PdCl_4$; even in the cold solution, a slow decomposition takes place. It may be used for the estimation of palladium, being decomposed when heated in an atmosphere of coal-gas, leaving a residue of palladium. A series of experiments have served to show that, by observing the above conditions, the amounts of platinum and palladium in a mixture of their chlorides may be accurately estimated. A. L.

Technical Analysis of Asphaltum. By LAURA A. LINTON (*J. Amer. Chem. Soc.*. 1896, **18**, 275—279).—The author gives a few more instructions as to the assay of asphaltum (Abstr., 1895, ii, 333). In estimating the moisture, the temperature should not exceed 50°, and the drying is best effected by heating the sample in a current of dry air; the dried sample is then tested as directed.

It is now recommended to fraction the asphaltene by estimating the portion soluble in boiling turpentine and that soluble in chloroform only. After removing the petrolene, the residue on the filter is digested in boiling turpentine until the filtrate is colourless; the filter is then washed with alcohol and dried at 100°. If a black semi-liquid substance separates from the mass, the extraction with turpentine should be repeated; the residue on the filter is finally exhausted with chloroform to remove the portion undissolved by the turpentine. "Aged" varieties of asphaltum contain a larger proportion of asphal-

tene, but the fraction soluble in turpentine is smaller, whilst that soluble in chloroform is larger. L. DE K.

**Estimation of Glucose in Urine.** By B. A. VAN KETEL (*Zeit. physiol. Chem.*, 1896, **22**, 278—280).—The method originally used in the estimation of sugar in milk may also be used for the estimation of sugar in urine which is also rich in uric acid, or contains proteid or blood. To 50 c.c. of the liquid, 4 c.c. of liquid phenol and 10 c.c. of a 10 per cent. aqueous solution of lead acetate are added, and the mixture shaken and filtered. The filtrate, to which are added the washings of the filter, the whole being brought up to 100 c.c., can then be examined for sugar by the polarimeter, or after removal of the lead, and dilution, by means of Fehling's solution. Osazone crystals can also be prepared. W. D. H.

**Estimation of Sugar in Blood.** By FREDERICK W. PAVY (*Proc. Physiol. Soc.*, 1896, 7—10.)—The importance of the estimation of sugar in blood correctly is obvious. The difficulties of the analysis are great, because the proteids present must first be got rid of by precipitation in a form that lends itself to thorough washing. The author's alcohol method still holds; but the last traces of proteid in the alcoholic extract are best got rid of by boiling with hydrated alumina. W. D. H.

**Polarimetric Estimation of Milk Sugar in Human Milk.** By PAUL THIBAULT (*J. Pharm.*, 1896 [6], **4**, 5—10.)—In the analysis of cows' milk, acetates of lead or mercury, or sodium metaphosphate may be used to precipitate the proteids and fat. In dealing with human milk, however, these reagents do not give a liquid clear enough for optical examination. The author finds that a solution, containing, in 1 litre, 10 grams of picric acid and 25 c.c. of glacial acetic acid, when added to an equal volume of human milk gives, after filtration, a perfectly clear liquid, in which the milk sugar can be easily estimated by the optical method. A method is also given for the determination of the volume occupied by the fats, &c., previously separated. (Compare Wiley and Ewell, Abstr., 1896, ii, 628.) M. W. T.

**Gravimetric Estimation of Sugars, especially of Maltose, by means of Fehling's Solution.** By HARTOG ELION (*Rec. Trav. Chim.*, 1896, **15**, 116—122).—In the estimation of sugars by Fehling's solution, it is always advisable to oxidise the cuprous oxide to cupric before reducing it in a current of hydrogen. (Compare Abstr., 1891, 368.)

Another error in the estimation is caused by the action of the alkali on the asbestos filter; this error may be eliminated to a large extent by taking the mean weight of the filter before and after the experiment.

A third error, due to a secondary decomposition of the Fehling solution, may be eliminated by making a blank experiment, using an equal quantity of water instead of the sugar solution.

The author finds that in the case of maltose the Fehling's solution is reduced at the end of 2 mins., so that longer boiling is unnecessary.

J. J. S.

**Rapid Process for the Detection of Formaldehyde in Milk.** By GEORGES DENIGÈS (*J. Pharm.*, 1896, [6], **4**, 193—195).—Ten c.c. of milk is diluted with water and, after the addition of two or three drops of acetic acid and some potassio-mercuric iodide, the solution is filtered. One c.c. of Schiff's reagent (magenta decolorised by sulphurous acid) is then added, and, after 10 mins., 2 c.c. of hydrochloric acid. The amount of formaldehyde present is indicated by the depth of the violet colour produced.

M. W. T.

**Estimation of Hydrocyanic Acid in Officinal Waters.** By CARL GLÜCKSMANN (*Chem. Centr.*, 1896, i, 329; from *Pharm. Post.*, **28**, 569—570).—The author has not succeeded in getting trustworthy results by Mohr's copper sulphate process, the end reaction being very uncertain. Other investigators also condemn the method.

L. DE K.

**Palmarosa Oil.** By EDUARD GILDEMEISTER and KARL STEPHAN (*Arch. Pharm.*, 1896, **234**, 321—330).—See this vol., i, 81.

**Estimation of the Constituents of a Mixture of Primary, Secondary and Tertiary Amines of the same Radicle.** By CHARLES GASSMANN (*Compt. rend.*, 1896, **123**, 313—315).—The method described was worked out with special reference to the ethylenediamines. The dried mixture is dissolved in a definite quantity of water, and an aliquot part is titrated with normal hydrochloric acid, using phenolphthaleïn as indicator. An equal volume is then mixed with one and a half times the volume of normal hydrochloric acid indicated by the first experiment, diluted with twice its volume of alcohol, cooled with ice, and titrated with normal sodium nitrite solution, using starch paste and potassium iodide as indicator.

If Mx, My, and Mz are the respective molecular weights of the mono-, di- and tri-amines, A the weight of the mixture taken, B the number of c.c. of normal acid, and C the number of c.c. of normal nitrite solution required by A, then x, y, and z, the respective quantities of the mono-, di-, and tri-amines present in A are given by the equations.

$$x = \frac{[(My - Mz)C + (BMz - 1000A)]Mx}{1000(My - Mx)}.$$

$$y = \frac{[1000A - BMz + C(Mz - Mx)]My}{1000(My - Mx)}.$$

$$z = \frac{(B - C)Mz.}{1000}$$

For the ethylenediamines Mx = 59·56, My = 85·90 and Mz = 111·84 and the equations become

$$x = 0{\cdot}12706B - (2{\cdot}27216A + 0{\cdot}02947C)$$
$$y = 3{\cdot}3114A - 0{\cdot}18517B + 0{\cdot}0859C$$
$$z = 0{\cdot}05592(B - C).$$

The results are accurate to 0·33 to 0·5 per cent. C. H. B.

**Qualitative Examination of Acetanilide.** By CHARLES PLATT (*J. Amer. Chem. Soc.*, 1896, **18**, 142—146).—The following tests are recommended : strong cold nitric acid gives a colourless solution which on gentle heating turns first yellow and then brownish-red, evolving oxides of nitrogen. The cold solution also gradually assumes a brown colour, and deposits red, acicular crystals having an odour of nitrobenzene. If the nitric acid solution is rapidly evaporated to dryness, an oily residue of decided odour is left, but on slow evaporation a crystalline residue of slight odour is obtained. Dilute nitric acid dissolves the acetanilide in the cold with separation of oily globules ; and this solution, on slow evaporation, gives a brown residue with slight purplish tint. When boiled with the dilute acid, a colourless solution is obtained, and pungent fumes are evolved.

Strong sulphuric acid dissolves the compound yielding a colourless liquid which is not affected by boiling. The cold solution gradually acquires a pink or even brown colour, gradually changing to orange when viewed by reflected light ; subsequently, tufts of delicate acicular crystals appear, and the liquid becomes colourless.

Sulphuric acid and potassium dichromate give a dark green solution. If the solution of the compound in strong sulphuric acid is diluted before adding the chromate, no reaction is at first obtained, but gradually a reddish-brown colour is developed, changing to a dark olive-green.

Hydrochloric acid, alone or in conjunction with potassium dichromate, gives no marked reaction, but if the compound is dissolved in hydrochloric acid and then mixed with a weak solution of chromic acid a dark green coloration is finally observed. Aqueous potash produces a blue precipitate in this solution.

Bromine water added to the hydrochloric acid solution yields a heavy yellowish precipitate of bromaniline ; chlorine water, or a solution of bleaching powder, yields, however, no precipitate but gives a dark blue coloration which soon fades. If, before adding the bleaching powder, a few c.c. of a saturated solution of phenol is added, a brownish red colour is produced which turns blue on adding ammonia.

Aqueous potash liberates aniline, and if chloroform is also added, the mixture on heating gives the characteristic isonitrile reaction.

Sulphuric acid and sodium nitrite produce a fine red colouration.

Ferric chloride gives no reaction. Zinc chloride at a temperature of 270° causes the formation of a small quantity of flavaniline, a yellow substance with a green fluorescence. After acetanilide has been boiled with dilute nitric acid and potassium nitrite, the liquid turns deep red on boiling it with Plugge's reagent (a solution of mercurous nitrate containing nitrous acid). By means of these tests, acetanilide may be distinguished from antipyrine and phenacetine. Antypyrine also differs from acetanilide in being precipitated by mercuric chloride.

L. DE K.

**Estimation of Caffeine.** By MOSES GOMBERG (*J. Amer. Chem. Soc.*, 1896, 18, 331—342).—See this vol., i, 129.

**Estimation of Caffeine.** By GEORGES (*J. Pharm.*, 1896 [6], 4, 58—59).—0·5 gram of the finely powdered sample is mixed with fine sand, and thoroughly extracted with a 1 per cent. solution of sodium salicylate. The liquid is evaporated to about 50 c.c., and then shaken with chloroform; on evaporating the chloroform, the caffeine is left in a state of purity.
M. W. T.

**Estimation of Caffeine in Tea.** By MARIUS L. Q. VAN LEDDEN HULSEBOSCH (*Chem. Centr.*, 1896, i, 332; from *Pharm. Centr.*, 36, 742).—Five grams of dry powdered tea is mixed with 1 gram of calcium hydroxide and heated with 100 c.c. of water on the water bath for 3 hours. After restoring the loss caused by the evaporation, the liquid is filtered and 50 c.c. of it is mixed with 0·5 gram of sodium carbonate. After filtering and evaporating the liquid to about 15 c.c., it is introduced into an extractor and submitted to the action of ether for 3 hours; the ethereal solution on evaporation leaves pure caffeine. The author thinks the process may be applied to coffee, cocoa and kola.
L. DE K.

**Testing Quinine.** By MELCHOIR KUBLI (*Chem. Centr.*, 1896, i, 224—225; from *Pharm. Zeit. Russ.*, 34).—The author (compare Abstr., 1896, ii, 550) proposes another test for the purity of quinine sulphate, based on the following interesting reaction. When a neutral solution of quinine sulphate is precipitated by means of sodium carbonate, the liquid becomes clear again on adding solution of sodium hydrogen carbonate; but on passing a current of carbonic anhydride, the quinine is precipitated as normal carbonate, the volume of which may be measured in a graduated tube.

The presence of the salts of other cinchona alkaloids (hydroquinine excepted) exercises a remarkable influence on the volume of the precipitate, also on its appearance. Several examples are given.
L. DE K.

**Estimation of Quinine Salts by Means of Sodium Nitroprusside.** By I. G. KRAMERS (*Rec. Trav. Chim.*, 1896, 15, 138—147).—On the addition of a solution of sodium nitroprusside to a solution of a neutral salt of quinine, small tarry drops separate, which collect on the sides and bottom of the vessel, and then gradually change to salmon-coloured needles. A dilute solution of quinine (1 in 100), when heated to 80° and then treated with the nitroprusside, yields no permanent precipitate at first, but on keeping at the same temperature for some time the salmon-coloured needles separate, and on cooling more crystals are formed, but no tarry matter. These needles have the composition $(C_{20}H_{24}N_2O_2)_4, Fe_2(CN)_{10}(NO)_2H_4 + H_2O$. They are insoluble in ether and benzene, sparingly soluble in cold alcohol, more readily in hot. They melt and decompose at 177—185°, and at the same time become blue. The moist crystals also turn blue when exposed to bright sunlight or when heated above 105°, and they are only slightly hygroscopic.

The only other alkaloid which gives a similar sparingly soluble compound with sodium nitroprusside is hydroquinine.

1·07 milligram of cinchonidine, 1·62 of quinidine, 2·68 of cinchonine, and 5·74 of homocinchonidine in 1 c.c. solution yield no crystalline precipitates. The method can therefore be made use of for testing the purity of quinine salts. The quinine is precipitated by means of the nitroprusside, and a few drops of ammonia are added to the filtrate, when, if the salt is pure, no precipitate will be formed. J. J. S.

**Estimation of the Alkaloids in Nux Vomica.** By C. C. Keller (*Chem. Centr.*, 1896, i, 228; from *Schweitz. Woch. Chem. Pharm.*, **33**, 452).—Twelve grams of the powdered beans is introduced into a 200 c.c. flask and 80 grams of ether and 40 grams of chloroform are added; after half an hour 10 c.c. of 10 per cent. ammonia is added, and the whole is shaken at intervals for half an hour. After adding 15—20 c.c. of water and thoroughly shaking, 100 c.c. of the ethereal mixture is poured off into a separating funnel and shaken with 50 c.c. of 0·5 per cent. hydrochloric acid, the shaking being repeated with another 25 c.c. The acid liquid is drawn off, and after adding excess of ammonia, it is agitated thrice with 30 c.c. of chloroform mixed with 10 c.c. of ether. This, on evaporation, yields the alkaloids from 10 grams of the beans. L. de K.

**Separation of the Proteids of Milk.** By A. Schlossmann (*Zeit. physiol. Chem.*, 1896, **22**, 197—226).—See this vol., ii, 62.

**Estimation of Albumin in Urine.** By Georges (*J. Pharm.*, 1896 [6], **4**, 108—110).—Mercier (*J. Pharm.*, [6], 515) has shown that in order to obtain accurate results the urine should be diluted with water, so that the quantity taken for analysis does not contain more than 0·1 gram of albumin. When much water has been added, the albumin shows a tendency to redissolve; this the author proves experimentally to be due to the dilution of the salts present in the urine.

He suggests a method of analysis in which a saturated solution of magnesium sulphate is used as a precipitant. M. W. T.

**New Process for Estimating Albumin in Urine.** By E. Riegler (*Chem. Centr.*, 1895, i., 332; from *Wien. Med. Bl.*, 1895, 761).—Ten grams of asaprol is dissolved in 100 c.c. of water, and 10 c.c. of hydrochloric acid and 5 c.c. of this solution are added to 50 c.c. of urine, and the whole heated to 60°. The precipitate is collected, washed with about 150 c.c. of water, pressed dry between filter-paper, and finally dissolved in 25 c.c. of N/10 potash. The difference in the refractive index of this solution and that of the potash by itself serves as a measure for the estimation of the albumin. Divided by 540, the amount of albumin in 50 c.c. of urine is obtained. If the urine is rich in albumin, a smaller quantity must be taken; if poor, a larger amount. (Compare Abstr., 1895, ii, 542.) L. de K.

# General and Physical Chemistry.

**Refraction and Density.** By Isidor Traube (*Ber.*, 1896, **29**, 2732—2742).—The expression $V_m = m/d = \Sigma nC + Cov = \Sigma nC + 25 \cdot 9$ (see Abstr., 1896, ii, 235) was termed by Kopp the apparent molecular volume, but the author prefers to call it the molecular vibration volume; it is composed of the true molecular volume $\Sigma nC$, which the author terms the atomic nucleus volume, and the molecular covolume *Cov.* The values of $V_m$ are obtained from density determination, whilst an expression for the value of $\Sigma nC$ is given by the Clausius-Mosotti theory of dielectrica; if $v$ is the actual volume occupied by spherical molecules, $k$ the dielectricity constant, and $\mu$ the refractive index for infinite wave-length,

$$v = (k - 1)/(k + 2) = (\mu^2 - 1)/(\mu^2 + 2),$$

the fraction of unit space actually occupied by a molecule is $\Sigma nC/V_m$, and it should be proportional to $(\mu^2 - 1)/(\mu^2 + 2)$ if the argument be valid. The values of $\Sigma nC \ (\mu^2 + 2)/V_m \ (\mu^2 - 1)$ have been calculated for a long series of saturated organic compounds, and are constant within very narrow limits, the mean values being 3·53 for Cauchy's constant A, 3·44 for the D line, and 3·460 for $H_a$; the values of $\Sigma nC$ are calculated from the atomic nucleus volumes $C = 9 \cdot 99$, $H = 3 \cdot 1$, and $O = 5 \cdot 5$. Consequently, the vibration volumes of the atoms calculated from molecular weight and density are equal to the atomic nucleus volumes or atomic refractions multiplied by constants which vary within narrow limits with the wave-length of the light.

The quantity $\mu - 1$ is the "loss of time" experienced by a ray in traversing a thickness of the substance, instead of an equally wide vacuous space which is traversed in unit time. The loss of time is also very strictly proportional to that fraction of the space filled by a substance which represents the molecular nucleus volume, so that $\Sigma nC/V_m \ (\mu - 1)$ is practically constant; this quantity has the mean values 2·086 for $H_a$, and 2·073 for D, and knowing the density of a given substance, it is possible to calculate with fair approximation the refractive indices for these rays. It is evident that the two above expressions involving $\Sigma nC$, $V_m$ and functions of $\mu$ are independent of the temperature.

On dividing the atomic vibration volumes stated above by 2·086 or 3·460, the atomic refractions for $H_a$ of the corresponding atoms for the Gladstone, or the Lorenz and Lorentz, formula respectively are obtained; the numbers thus got for the simple formula agree more closely with the numbers in use than do those for the theoretical formula. By applying the formula $\Sigma nC \ (\mu^2 + 2)/V_m(\mu^2 - 1)$ to unsaturated compounds, it is possible to calculate the increments of molecular refraction due to double linkings between the carbon atoms with very fair approximation. W. J. P.

**Action of Light on Dyed Colours.** Report of British Association Committee, Section B, Liverpool, 1896 (*Chem. News*, 1896, **74**,

205—207, 218).—The report refers to blue and green colouring matters on wool and silk exposed to light under glass with free access of air and moisture, and examined by comparison with standards at various intervals; a very large number of samples were examined and the general results are tabulated under five classes:—I, Very Fugitive; II, Fugitive; III, Moderately Fast; IV, Fast, and V, Very Fast Colours. Interesting comments and notes are also given. D. A. L.

**Cadmium Standard Cell.** By WILHELM JAEGER and R. WACHSMUTH (*Ann. Phys. Chem.*, 1896, [2], **59**, 575—591).—The use of cadmium in place of zinc for the construction of standard cells of the Clark type has been proposed on account of the reduction that is thus attained in the temperature coefficient of the cell. The authors have submitted this point to further investigation, and have also ascertained the ratio of the E.M.F. of the cadmium cell to that of the Clark cell, and the influence of impurities and of time on the constancy of the cadmium cell. The cell is best made of the usual H pattern, with electrolytically amalgamated platinum electrodes sealed through the glass. In place of pure cadmium, an amalgam of 1 part by weight of cadmium to 6 parts of mercury is used (m. p. 60°). The mercurous sulphate is mixed with crystals and a concentrated solution of cadmium sulphate and some mercury to a thick paste, and this paste is placed over the mercury of the positive pole. The negative pole (1Cd : 6Hg) is covered with a layer of cadmium sulphate crystals, and the rest of the cell is then filled with a concentrated solution of cadmium sulphate. The E.M.F. of this cell at 20° is 1·019 volt. The change in E.M.F. with change in temperature between 5° and 25° is expressed by the equation

$$E_t = E_{20} - 3{\cdot}8 \times 10^{-5}\,(t-20) - 0{\cdot}065 \times 10^{-5}\,(t-20)^2,$$

and is, therefore, for 1°, only about $\frac{4}{1000}$ per cent. In the effect of the influence of impurities and in durability, the cadmium cell was found to be in no way inferior to the Clark cell. H. C.

**Heat of Formation of Lithium Hydride.** By ANTOINE GUNTZ (*Compt. rend.*, 1896, **123**, 694—696. Compare Abstr., 1896, ii, 359).—The heat of formation of lithium hydride was calculated from the heats of dissolution of the hydride and of the metal itself in water.

Heat of dissolution of lithium hydride in water at 18° = +31·6 Cal.

Heat of dissolution of lithium in water at 18° = +53·2 Cal.

Therefore, Li solid + H gas = LiH solid = +21·6 Cal., a number which explains the stability of the compound.

The fact that the above value for the heat of dissolution of lithium in water is much greater than that obtained by Thomsen, namely, +49·08 Cal., is attributed by the author to the much greater purity of the metal used by him. The heats of formation of lithium compounds deduced from Thomsen's number are accordingly too low. Lithium hydride melts at 680°, at which temperature its tension of dissociation is about 27 mm. At ordinary temperatures, dry chlorine has no action on it; when heated in a current of that gas to a dull red heat, it burns, giving lithium chloride and hydrogen chloride. At a red

heat, hydrogen chloride acts on it, forming lithium chloride and hydrogen.

It reacts slowly with absolute alcohol, but is without action on dry benzene, toluene, or petroleum, at ordinary temperatures. Lithium hydride differs markedly in its properties from the hydrides of sodium and potassium. A. C. C.

**Thermochemistry of Cyanamide.** By PAUL LEMOULT (*Compt. rend.*, 1896, **123**, 559—562).—The cyanamide used was prepared by the action of mercuric oxide on thiocarbamide, and its molecular weight was determined by cryometric observations on its solution in acetic acid. Combustion in the calorimetric bomb gives 4090 Cal. as the heat of combustion of 1 gram; the molecular heat of combustion is, therefore, 171·78 Cal. at const. vol., and 171·5 Cal. at const. pressure, the heats of formation from its elements being −8·4 Cal. and −8·2 Cal. respectively. Its heat of dissolution in water is −3·59 Cal., and hence its heat of formation in solution is −12·0 Cal., a result which explains the greater stability of the compound when in the solid state.

From these data, it follows that the action of mercuric oxide on thiocarbamide develops +25·2 Cal., whilst the conversion of cyanamide in dilute solution into carbamide would develop +20·2 Cal.

The addition of dilute acids to solutions of cyanamide causes no thermal disturbance, but the heat of neutralisation by potassium hydroxide (one molecular proportion) is +3·79 Cal., and by sodium hydroxide +3·6 Cal. In either case, the addition of a second molecular proportion of alkali causes a slight development of heat, but a third proportion has no effect. The heat of neutralisation by ammonia is +1·38 Cal. It follows that in aqueous solution cyanamide behaves as an acid, the energy of the acidic function being comparable with that of hydrocyanic acid. It would seem also that there is a difference between the functions of the two replaceable atoms of hydrogen.

C. H. B.

**Thermochemistry of Hexamethylenetetramine and its Nitroso-derivatives.** By MARCEL DELÉPINE (*Compt. rend.*, 1896, **123**, 650—653).—The heat of combustion of pure hexamethylenetetramine, determined by burning in the calorimetric bomb, is 1006·53 Cal. (const. press.), and its heat of formation from its elements −26·73 Cal.

Its heat of dissolution in water at 15° (1 mol. in 1·5 to 2·5 litres of water) is 4·8 Cal., from which the heat of formation of dissolved hexamethyleneamine is −21·93 Cal. In order to verify the accuracy of the latter number, it was employed in calculating the heat of formation of hexamethylenetetramine dinitrate, and the result, 92·3 Cal., compared with that obtained by direct experiment +92·94 Cal.

It is incidentally remarked that hexamethylenetetramine dinitrate (47·37 per cent. $HNO_3$) gives, on combustion, very little nitric acid.

*First Nitroso-derivative*, $(CH_2)_5(NO)_2N_4$.—Heat of combustion (const. press.) = 872·28 Cal., from which its heat of formation (cryst.) is found to be −55·78 Cal.

*Second Nitroso-derivative*, $(CH_2)_4(NO)_4N_4$ (compare Abstr., 1889, 33).

—Heat of combustion (const. press.) = 745·96 Cal., from which its heat of formation is found to be $-91·76$ Cal.

The replacement, therefore, of $CH_2$ by $(NO)_2$ diminishes considerably the heat of formation of these substances, and renders it strongly endothermic, the second substitution producing a greater diminution than the first. The nitroso-derivatives are much less stable than the base itself. A. C. C.

**Dependence of the Dissociation of some Acids on Temperature and the Heat of Dissociation.** By HANS EULER (*Zeits. physikal Chem.*, 1896, **21**, 257—271).—Determinations of the conductivity were made by Kohlrausch's method in the case of benzoic, toluic, salicylic, metahydroxybenzoic, ortho- and meta-nitrobenzoic, and dichloracetic acids, at various temperatures between 10° and 50°, and at various dilutions. Interpolation formulæ were calculated which, in almost all cases, except with the sodium salts, were of the form $\lambda = a + bt - ct_2$, indicating the occurrence of a maximum (compare Jahn and Schröder, Abstr., 1895, ii, 203). From these values, the dissociation constants are calculated at the different dilutions and temperatures, the values from the different dilutions agreeing satisfactorily with one another, except in the case of orthonitrobenzoic acid and dichloracetic acid, where, however, the value at 0° was undoubtedly higher than that at 25°, results not in accord with those of Wildermann. In all cases, the dissociation constant is a function of the temperature, a maximum occurring for benzoic acid at about 35°, and for metahydroxybenzoic acid at about 28°. For orthotoluic acid, the values decrease continuously as the temperature rises, but increase for salicylic and metanitrobenzoic acids. Calculation of the heat of dissociation of the acids proved it to invariably increase with rise of temperature. In most cases, it is at first negative, the temperature at which zero is reached being that of the maximum dissociation, a relation indicated by the expression $Q = 0·50804\ T^2.1/k.dk/dt.$ from which the values are calculated.

L. M. J.

**The Determination of Molecular Weights. IV.** By ERNST O. BECKMANN (*Zeits. physikal. Chem.*, 1896, **21**, 239—256).—The paper contains further details of the apparatus and methods employed by the author. An electromagnetic stirrer is described, for use in freezing point determinations, whereby the apparatus can be kept completely closed and the entrance of moist air avoided, an important precaution when phenol or acetic acid are employed as solvents. A form of boiling point apparatus is described, small tetrahedra of platinum foil being recommended for the prevention of bumping; and the author states that in the Beckmann thermometers a *conical* junction of the capillary tube to the reservoir is necessary. Experiments are recorded indicating the availability of the apparatus as described, aniline, water, chloroform, ether, ethylic alcohol, and benzene being employed as solvents (comp. Abstr., 1895, ii, 154, 382; 1896, ii, 236). L. M. J.

**Exact Cryometry: Application to Sodium Chloride Solutions.** By FRANÇOIS M. RAOULT (*Compt. rend.*, 1896, **123**, 475—478).

—The author has made several series of determinations of the freezing points of solutions of sodium chloride, using the apparatus previously described (*Compt. rend.*, 1896, **122**), but employing ether instead of carbon bisulphide. It was found that the temperature could be kept constant to 0·1° at any point between – 15° and the surrounding temperature for several hours. In the following table, P is the weight of salt in 100 grams of water; C, the apparent reduction when the converging temperature is 3·5° below the freezing point; $C_0$, the real reduction when the converging temperature and the freezing point coincide.

| P | $C_1$ | $C_0$ | $C_1—C_0$ | $C_0 \times 0·002$ |
|---|---|---|---|---|
| 5·850 | 3·4435 | 3·4381 | 0.0054 | 0·0068 |
| 2·859 | 1·6880 | 1·6839 | 0·0041 | 0·0034 |
| 1·400 | 0·8286 | 0·8267 | 0·0019 | 0·0017 |
| 0·690 | 0·4132 | 0·4111 | 0·0021 | 0·0008 |
| 0·341 | 0·2107 | 0·2093 | 0·0014 | 0·0004 |
| 0·176 | 0·1113 | 0·1111 | 0·0002 | 0·0002 |

$C_0 \times 0·002$ and $C_1—C_0$ are practically identical, and hence $C_1—C_0 = C_0 \times 0·002$ or $C_1 = C_0(1 + 0·002)$, and the general expression $C_1 = C_0(1 + q)$ previously arrived at (q having always a very small value) is experimentally verified for sodium chloride solutions.

The real and apparent molecular reductions can be calculated from the figures in the table; the limiting value is 38·05 for the former and 37·88 for the latter. The curves, with the observed reductions for abscissæ and molecular reductions for ordinates, are very similar in the two cases, and cut the axis of the ordinates at practically the same point, which corresponds with the limiting molecular reduction. The experiments with sodium chloride, therefore, confirm the author's previous conclusion that the temperature of the surroundings has no influence on the laws relating to the reductions of the freezing point of different solutions of the same substance.

The real molecular reductions given in the table correspond to a superfusion of 0·5°, and the absolute values, when the concentration is not altered by freezing, are obtained by multiplying the figures by 0·994. The limit molecular reduction for sodium chloride is then found to be 37·82, which is identical with that requiring complete ionisation.

The different results obtained by Ponsot (Abstr., 1896, ii, 411, 636) are attributable to insufficient agitation of the liquid, especially in a vertical direction. C. H. B.

**Exact Cryometry: A Correction.** By FRANÇOIS M. RAOULT (*Compt. rend.*, 1896, **123**, 631—632).—After some reference to an earlier paper (preceding abstract), it is remarked that, in the determination of the true depression of the freezing point, absence of radiation is not theoretically necessary, which is fortunate, since that condition is absolutely incapable of realisation, owing to the development of heat produced by the agitation of the liquid. A. C. C.

**Expansion during the Dissolution of Ammonium Salts and of Sodium Thiosulphate.** By HUGO SCHIFF and U. MONSACCHI

(*Zeits. physikal. Chem.*, 1896, **21**, 277—296).—The expansion occurring during the dissolution of ammoniacal salts was first determined, pyknometers of 25 c.c. and 50 c.c. capacity being employed. In the case of ammonium nitrate, the expansion (throughout referred to 100 parts of the mixed constituents) was found to vary from 4·0 for a 63 per cent. solution to 0·179 for a 4 per cent., with a minimum of 0·119 at 7 per cent. As the expansion may be due to a dissociation into ammonia and nitric acid, the effect of dissolution in dilute nitric acid was determined, but the expansion was found to be even greater than in aqueous solution, a result also obtained by dissolution in potassium nitrate and ammonium chloride solutions. The expansion may be fairly well calculated by assuming that a saturated solution of the ammonium nitrate is first formed, and then mixed with a solution containing the other salt and the remaining water. In methylic alcohol, however, a contraction of about 0·86 occurs for the saturated solution (14 per cent.). Ammonium chloride gave an expansion of 2·6 at 30 per cent. and 0·46 at 10 per cent., that of ammonium bromide being in each case slightly lower. In the case of ammonium iodide, however, contraction occurs, varying from 1·4 at 60 per cent. to 0·035 at 3 per cent., and is greater in alcohol than in water. Hydroxylamine hydrochloride gave an anomalous result, contraction first occurring reaching a maximum at from 10 to 15 per cent. with normal volume at 28 per cent., after which expansion occurs, whilst in the case of hydrazine hydrochloride a perfectly regular contraction obtains. Sodium thiosulphate gave results very similar to that of the hydroxylamine salt, the maximum contraction occurring at 40 per cent. and zero at 78 per cent., after which expansion occurs, the values being not quite concordant with those of Boisbaudran (Abstr., 1895, ii, 486), partly owing to the latter using a higher sp. gr. for the solid salt (1·752) than that obtained by the authors (1·734). L. M. J.

**Laws of Irreversible Processes.** By LADISLAUS NATANSON (*Zeits. physikal. Chem.*, 1896, **21**, 193—217).—A mathematical paper, unsuitable for abstraction, in which the author deduces expressions for the velocity of various irreversible processes, such as diffusion, heat conductivity, dissipation of electrical energy. L. M. J.

**Relationship of the Rate of Diffusion to the Initial Concentration of Dilute Solutions.** By W. KAWALKI (*Ann. phys. Chem.*, 1896, [2], **59**, 637—651).—Nernst has shown, as a consequence of the dissociation theory, that the rate of diffusion of dissolved substances should alter very little with the concentration when the solutions reach a certain degree of concentration. In former experiments (Abstr., 1894, ii, 345), the author found that with very small initial concentrations the values calculated for the diffusion coefficient $k$ do not correspond with one another, and it was pointed out that the behaviour was probably due to convection currents. Careful experiments with dilute solutions of sodium acetate and carbamide have since served to confirm this view and support Nernst's conclusions. The diffusion coefficient, $k_1$ for dilute alcoholic solutions was also determined, and the ratio $k_1/k$ found for sodium acetate = 2·19, and for carbamide = 1·79. H. C.

**Determination of Isosmotic Concentrations.** By SVEN G. HEDIN (*Zeits. physikal. Chem.*, 1896, **21**, 272—276).—Chiefly a controversial paper and a criticism of Köppe's results (Abstr., 1895, ii, 208). The author considers that errors occur in Köppe's work owing to (1) the use of salts which directly affect the blood corpuscles, (2) the use of standard solutions which are not actually isosmotic, whilst, further, he considers it necessary to defibrinate the blood employed.

L. M. J.

**Explosive Properties of Acetylene.** By MARCELLIN P. E. BERTHELOT and PAUL VIEILLE (*Compt. rend.*, 1896, **123**, 523—530).—When acetylene under ordinary pressure is subjected to the action of an electric spark, a red-hot wire, or a discharge of fulminate, the decomposition of the gas does not extend beyond the immediate neighbourhood of the source of decomposition, but under pressure the results are different, and when the pressure exceeds two atmospheres the gas shows the ordinary properties of explosive mixtures. Under these conditions, if decomposition is produced at any point by one of the methods indicated, it very rapidly spreads through the whole mass of the gas, which is thereby resolved into hydrogen and bulky pulverulent carbon. Under an initial pressure of 21 kilos. per square cm., the pressure developed by the decomposition is 10 times as great, and the change is complete in 0·018 of a second. The ratio of the final to the initial pressure decreases, and the time required for complete decomposition increases, the lower the pressure. Even with an initial pressure of 21 kilos. per square cm., the rate of propagation of the change is much below the velocity of the explosive wave in the oxyhydrogen mixture. The calculated temperature of decomposition is 2750°, and the calculated pressure 11 times as great as the initial pressure. The observed pressure agrees fairly well with the calculated.

Liquefied acetylene decomposes in the same way as the gas; with 18 grams of the liquid in a bomb of 48·96 c.c. capacity, the final pressure was 5,564 kilos per square cm., and under these conditions the explosive force is nearly equal to that of guncotton. The decomposition of the liquid is, however, relatively slow when excited by simple ignition. When the bomb contains both liquid and gas, there is a change in the curve of pressure which indicates two distinct phases of the explosion, one most probably corresponding with the decomposition of the gaseous part, and the other, which lasts longer and raises the pressure much higher, to the decomposition of the liquid portion.

Mere shock, such as is caused by a fall from a considerable height, seems incapable of causing the explosion of either compressed or liquefied acetylene. If the vessel breaks there is still no explosion in the case of the compressed gas; but if the vessel contains liquid acetylene, the fracture is followed after a short interval by an explosion. The latter, moreover, differs essentially from the explosive decomposition of the gas, and is not accompanied by the separation of free carbon; it results from the admixture of air with the acetylene, and the ignition of this mixture by sparks that result from the friction of the breaking metal.

If, however, liquid acetylene is decomposed by the discharge of a

small quantity of fulminate contained in the same vessel, violent detonation takes place, and the fragments of the vessel have the appearance of those produced by a true explosion. All the fragments are covered with the carbon liberated from the gas.

In the action of small quantities of water on excess of calcium carbide in a closed vessel, there may be sufficient local elevation of temperature to initiate the decomposition of the whole of the compressed gas. This local elevation of temperature may also produce polymerides, which are themselves endothermic. Other causes of dangerous local heating are too rapid compression, or the local pressure that arises when the gas is allowed to escape very suddenly from a vessel in which it is highly compressed. The precautions needed to prevent accidents arising from these causes are obvious. C. H. B.

**Influence of Pressure on the Inversion Constants of some Acids.** By O. STERN (*Ann. Phys. Chem.*, 1896, [2], **59**, 652—663).—The change in the conductivity of electrolytes with an increase in the external pressure has been accounted for on the supposition that the rise in pressure produced an increase in the electrolytic dissociation. Röntgen found, however, that an increase in the pressure does not accelerate, but retards, the rate of inversion of cane sugar by hydrochloric acid. The author has extended Röntgen's observations, and finds that the rate of inversion of solutions containing 23 grams of cane sugar per 100 c.c., and varying amounts of hydrochloric, sulphuric, or oxalic acid, is always reduced when the external pressure is increased from 1 to 500 atmospheres. The influence of the pressure on the rate of inversion is smaller, the smaller the amount of acid added. If the inversion is brought about by phosphoric or acetic acid, the reverse is true, as pressure here increases the rate of inversion, and this increase is the greater, the greater the amount of acid added. The rate of inversion decreases somewhat as the concentration of the sugar solutions is decreased, but the change in the rate of inversion with the pressure remains about the same. A rise in temperature of about 10° produces a very marked increase in the rate of inversion, but here, again, the effect of an increase of pressure remains about the same.

H. C.

**Crystal Symmetry.** By VIKTOR VON LANG (*Zeits. physikal. Chem.*, 1896, **21**, 218—224).—The author draws attention to the simple method which he used many years ago in his *Lehrbuch der Krystallographie* (Wien, 1866) for deducing the thirty-two possible types of crystal symmetry from fundamental crystallographic laws; the argument is restated and its simplicity urged in favour of its more general use. A system of nomenclature for the thirty-two crystal systems is proposed, which has the advantage over many others that the names indicate immediately the prominent characteristics of the types of symmetry they are intended to describe. W. J. P.

**Atomic Weights of the Elements.** By DELAUNEY (*Compt. rend.*, 1896, **123**, 600—603).—The author arranges the elements in four groups, according as their atomic weights, expressed by the nearest

whole numbers, are 0 + a multiple of 4, 1 + a multiple of 4, 2 + a multiple of 4, or 3 + a multiple of 4. The first group is the largest, and the elements in it can be arranged in three columns, the successive members in each of which differ from the element at the top (C (12), Ce (92), or $x$ (172) by 4, 8, 4, 4, 8, 4, 4, 4, 4, 24. There are gaps due to undiscovered elements or to inaccurate determinations of known elements. The next largest class contains elements whose atomic weights are 3 + a multiple of 4, and here there are two columns, the successive members of which differ from the first in the same way as in the first group, but only three known elements are contained in the second column. On the other hand, several elements that properly belong to this group do not fit into the columnar arrangement. The group 2 + a multiple of 4 contains eight elements which, starting from the first, helium, increase by 12, 56, 20, 16, 20, 56, 12, whilst the three elements in the groups 1 + a multiple of 4 increase after the first (Be) by 56 and 20. A certain number of the less known elements do not fit into any of these groups. C. H. B.

**Hypothesis of the Atomic Motion of the Elements and their Genesis.** By Flavian Flawitzky (*Zeits. anorg. Chem.*, 1896, **12**, 182—187).—The author advances the hypothesis that the atoms of an element move in curves which lie in planes parallel to one another. The atoms of different elements move in planes which are inclined at certain definite angles to one another. The orientation of the motion determines the character of the element, and can be regarded as due to the influence of some selective dualistic force, such as electricity, in the formation of the element. H. C.

**A New Form of Turbine for Use in Laboratories.** By George F. Jaubert (*Bull. Soc. Chim.*, 1896, [3], **15**, 9—10).—The author describes a new form of turbine for use in laboratories supplied with water under high pressure. The turbine is designed for carrying out operations on a moderate scale. No details are given with regard to construction. M. W. T.

---

## Inorganic Chemistry.

**Slow Oxidation of Hydrogen and Carbon.** By H. Hirtz and Victor Meyer (*Ber.*, 1896, **29**, 2828—2831. Compare this vol., ii, 19).—It is improbable that ozone was formed in the earlier experiments (*loc. cit.*), as the gas evolved when dilute sulphuric acid acts on potassium permanganate is quite inert, and ozone appears to be produced only when the concentrated acid is employed.

Morse, Hopkins, and Walker have shown (Abstr., 1896, ii, 475) that, under certain conditions, finely divided manganese dioxide effects the reduction of potassium permanganate, oxygen being liberated. These conditions, however, were not those employed in the above

experiments, and again only in the acidified permanganate was any appreciable residue observable. Later experiments have shown that acidified permanganate solutions in contact with manganese dioxide yield only 12·5 per cent. of the volume of gas obtained when hydrogen is present,

The difference in volume between the amount of oxygen obtained when the permanganate solution is quiescent, and when it is strongly agitated, has suggested the idea that the action is a reversible one; experiments made with the object of observing any absorption of oxygen under the conditions employed have given negative results, thus rendering the suggestion improbable. A. L.

**Purification of Water by Distillation.** By GEORGE A. HULETT (*Zeits. physikal. Chem.*, 1896, **21**, 297—301).—The author recommends the use of a condenser containing an inner tube of platinum, narrowed slightly at the lower end, and with the upper end projecting about 15 cm. into the neck of the retort employed for the distillation. The space between the platinum tube and the neck of the retort is packed with asbestos, and by this means only the water actually condensed in the platinum tube is collected. Ordinary distilled water which had been allowed to remain over potassium permanganate or potassium dichromate and sulphuric acid, when distilled over barium hydroxide in this apparatus, gave a distillate of speedily diminishing conductivity, the value $0·76 \times 10^{-10}$ being reached before one-fourth of the water had distilled. No barium hydroxide appears to be carried over, but, if it is not employed, sulphuric acid may occur in the distillate.

L. M. J.

**Nitrites in the Air.** By GEORGE DEFREN (*Chem. News*, 1896, **74**, 230—231).—Re-distilled water, free from ammonia, nitrites, and nitrates, was exposed to the air in well-ventilated rooms, in porcelain evaporating dishes 15 cm. in diameter; each dish contained 100 c.c. of the water, the superficial area exposed being 95 sq.cm. The water was examined at intervals for nitrites, the quantity being computed by comparison with a standard solution of potassium nitrite containing, per c.c., 0·0000001 gram of nitrogen as nitrite, the conditions as regards burning gas jets and lamps being noted. Under varying conditions, the quantity of nitrite, in terms of c.c. of standard, found, after one hour, was 2·5, 3·5 and 8; after two hours, 3·5, 8·5 and 13·5; after seventeen hours, in the last instance, 84·2; and after nineteen hours, in the first and second instance, respectively 57·2 and 72·7. The results show that, where gas is burning, nitrites exist in the air even in well-ventilated rooms, and that water absorbs these nitrites in quantities increasing with the time of exposure to the polluted air. D. A. L.

**Tetrametaphosphimic Acid.** By HENRY N. STOKES (*Amer. Chem. J.*, 1896, **18**, 780—789. Compare this vol. ii, 28.)—*Tetrametaphosphimic acid*, $P_4N_4O_8H_8 + 2H_2O$, is best prepared by the action of water on tetraphosphonitrilic chloride, $P_4N_4Cl_8$, dissolved in ether free from alcohol. Chlorhydrins are formed as intermediate products, but remain dissolved in the ether, the acid crystallising in needles from

the aqueous portion. The oily chlorhydrins, when separated, and warmed with dilute hydrochloric acid, yield the acid, crystallising in colourless needles. One hundred parts of water at 20° dissolve 0·64 part of the crystallised acid; it is somewhat more soluble in boiling water, but insoluble in alcohol. Boiling alkaline solutions cause no evolution of ammonia, and heating with moderately strong hydrochloric or nitric acids brings about but little decomposition. The water of crystallisation is not given off in a vacuum over sulphuric acid, but when heated at 100° the crystallised acid loses weight rapidly, although the theoretical loss is never reached owing to intramolecular changes, in which a portion of the water takes part. It forms three series of salts, $P_4N_4O_8H_6M'_2$, $P_4N_4O_8H_4M'_4$, and $P_4N_4O_8M'_8$.

*Dipotassium tetrametaphosphimate*, $P_4N_4O_8H_6K_2$, was prepared by adding excess of acetic acid to a solution of the acid in cold, dilute caustic potash. On warming, the salt is deposited as a heavy, sandy powder, consisting of microscopic, thick, rectangular (? quadratic) prisms with basal planes; it is very sparingly soluble, even in boiling water. The *tetrapotassium* salt, which is very soluble, forms large, flat, obliquely-terminated plates. The *tetrasodium* salt, $P_4N_4O_8H_4Na_4 + 2\frac{1}{2}$ (?) $H_2O$, forms obliquely-terminated, flat prisms; it is sparingly soluble in cold, but readily in hot water.

The *tetrammonium* salt, $P_4N_4O_8H_4(NH_4)_4 + 4H_2O$, is obtained by treating the acid with strong ammonia, and usually forms well-developed, flat, monoclinic prisms; it dissolves readily in water, but with difficulty in strong ammonia. The *diammonium* salt, $P_4N_4O_8H_6(NH_4)_2$, is precipitated from a solution of the neutral salt on strongly acidifying with acetic acid and warming; it forms four- and six-sided prisms (? tetragonal), and is very sparingly soluble, even in boiling water. The *barium* salt, $P_4N_4O_8H_4Ba_2 + 2H_2O$, forms microscopic needles. No definite results were obtained in the attempt to prepare a magnesium salt. The *manganese* salt forms characteristic, pink, rectangular plates. Ferric chloride when added to a dilute solution of the neutral ammonium salt gives, on warming, a white, amorphous precipitate soluble in much warm hydrochloric acid. The *tetra-silver* salt, $P_4N_4O_8H_4Ag_4$, is obtained on adding a solution of silver nitrate to one of the free acid. When the precipitation takes place in the cold, the salt is granular or amorphous, but is crystalline when formed in hot solutions. The *octo-silver* salt, $P_4N_4O_8Ag_8$, is obtained as a yellowish, flocculent precipitate when an ammoniacal solution of the acid is added to an excess of silver nitrate; on the other hand, a solution of a neutral tetrametaphosphimate added to an ammoniacal silver nitrate solution, produces a white, flocculent precipitate. If a solution of the latter in ammonium nitrate is boiled, an orange-yellow, semicrystalline precipitate is formed. The white and the yellow compounds give on analysis almost the same numbers, and are regarded as tautomeric forms corresponding with the acids $[PN(OH)_2]_4$ and $(PO\cdot NH\cdot OH)_4$. The author discusses the probable constitution of tetrametaphosphimic acid, and calls attention to the fact that, in its general properties, it differs markedly from the trimetaphosphimic acid previously described by him. A. C. C.

**Uniformity of the Distribution of Argon in the Atmosphere.** By TH. SCHLŒSING, JUN. (*Compt. rend.*, 1896, **123**, 696—697. Compare Abstr., 1896, ii, 166 and 219).—The author has made determinations of argon in samples of air collected in places widely separated, and taken at various distances (a few metres to 2,275 m.) from the earth's surface. His numbers, which are very concordant, show that argon is uniformly distributed in the atmosphere, and that every 100 volumes of the mixed nitrogen and argon contain 1·192 volumes of the latter gas. This is in strict accordance with his previously published number.

A. C. C.

**A Method of Preparing Double Silicates of Potassium and other Metals.** By ANDRÉ DUBOIN (*Compt. rend.*, 1896, **123**, 698—700).—By dissolving a mixture of magnesia and silica in fused potassium fluoride and then submitting the product to prolonged fusion with potassium chloride, the author has obtained both a double silicate of magnesium and potassium, and two compounds containing fluorine in addition,

$$4KF,SiO_2 + 3MgO,2K_2O,10SiO_2 \text{ and } 2MgF_2,SiO_2 + 4(K_2O,MgO,3SiO_2)$$

(see Abstr., 1895, ii, 351). Beryllium oxide dissolves in fused potassium fluoride, and when submitted to the treatment described above, gives a crystalline product which appears to be homogeneous, but really consists of a mixture of isomorphous compounds. These are not analogous in composition to the double silicates of magnesium and potassium, but vary between $2K_2O,3BeO,7SiO_2$ and $2K_2O,3BeO,5SiO_2$; moreover, no double silicates containing fluorine could be prepared as in the case of magnesium. On adding baryta to fused potassium fluoride containing dissolved silica, a crystalline double silicate having the formula $K_2O,2BaO,3SiO_2$ (sp. gr. = 3·78) was obtained. If this mixture is fused with potassium chloride, three compounds are formed, the principal one having the formula $K_2O,7BaO,8\ SiO_2$, but containing a little fluorine. Double silicates could not be prepared in the case of calcium, the products always containing chlorine or fluorine; mixtures of crystalline products were obtained, only one of which, having the formula $4KF + K_2O,5CaO,6SiO_2$, could be isolated. A. C. C.

**Rubidium Dioxide.** By HUGO ERDMANN and PAUL KÖTHNER (*Annalen*, 1896, **294**, 55—71).—The authors have investigated the inflammable nature of metallic rubidium, in order to ascertain whether the spontaneous combustion of this substance on exposure to air, observed by Bunsen in 1863, is due to the influence of oxygen or of moisture.

The methods hitherto adopted for the production of metallic rubidium are very unsatisfactory, and the authors describe a convenient and safe process by which 85 per cent. of the theoretical quantity of the metal may be obtained from rubidium hydroxide. A seamless iron tube, of 15 mm. bore, 1 metre in length, having walls 3 mm. thick, is bent at an angle of 125° about 15 cm. from one end, fitted at the elbow with a loose plug of clean, long, steel shavings, and heated to redness while a current of hydrogen is passed through it; 20 grams of

freshly fused, anhydrous rubidium hydroxide is rapidly crushed to a coarse powder with magnesium filings (10 grams), in a warm mortar, and transferred to the long arm of the tube. This is placed in a small combustion furnace, with the short arm dipping beneath the surface of paraffin oil in a porcelain vessel, a gentle current of hydrogen, free from arsenic and dried by means of sulphuric acid and phosphoric anhydride, being passed through the tube; the temperature is cautiously raised, the application of heat being interrupted as soon as the increase in the current of gas indicates that the action has begun. When hydrogen is no longer evolved from the rubidium hydroxide, the temperature of the tube is raised to a red heat, and after half an hour the metal distils over, 14 grams being obtained from the quantity of hydroxide mentioned. When obtained in this manner from rubidium hydroxide prepared from ferric rubidium alum (Erdmann, Abstr., 1894, ii, 351), the metal is in a highly purified condition, and forms a convenient source of salts required for physical investigations; it melts at 38·5°, and has a sp. gr. = 1·5220 at 15°.

*Rubidium dioxide*, $RbO_2$, is obtained by the action of dried oxygen on the metal at common temperatures. In view of the fact that burning rubidium attacks glass, porcelain, platinum, silver, and rubidium chloride, it is necessary to allow the metal to fall into an aluminium dish which lies in a small glass flask filled with nitrogen; the whole apparatus is then weighed, and when the metal is converted into oxide, it is again filled with nitrogen, and weighed. The metal quickly melts when a stream of oxygen plays on it, and becomes ignited if the current of gas is not checked; when the oxidation proceeds in a normal manner, however, the metal preserves for some time the appearance of molten gold, but finally swells and becomes black, and then ceases to absorb the gas. On raising the temperature to 500°, it again begins to absorb oxygen, probably owing to the presence of metallic particles previously protected by oxide from the action of the gas, the volume becomes reduced, and a viscous, black liquid is produced; after this stage has been reached, no more oxygen is absorbed, and on cooling the apparatus, the oxide crystallises in dark brown plates. The authors have obtained no evidence of the existence of other oxides of rubidium, and the dioxide they describe may be heated at a high temperature without losing or absorbing oxygen; it acts violently on water, however, yielding rubidium hydroxide and hydrogen peroxide, oxygen being liberated. When rubidium dioxide is gently heated in an atmosphere of hydrogen, rubidium hydroxide, water, and oxygen are produced, a result which the authors attribute to the intermediate formation of hydrogen peroxide, in accordance with the equation $2RbO_2 + 2H_2 = 2RbOH + H_2O_2$; if the action proceeds at too high a temperature, violet light is developed, less water is formed, and the aluminium dish is corroded, rubidium aluminate, $RbAlO_2$, being produced.

It is convenient to employ an aluminium dish for the preparation of rubidium dioxide, because this metal is not wetted by molten rubidium, and it also resists the action of the fused dioxide at temperatures below 500°.

M. O. F.

**Double Salts of Rubidium.** By HUGO ERDMANN and PAUL KÖTHNER (*Annalen*, 1896, **294**, 71—79. Compare Abstr., 1894, ii, 351).—Ferric rubidium, ferric ammonium, and ferric potassium alums melt respectively at 53°, 43—44°, and 33°, and comparison of rubidium double salts with the analogous ammonium salts reveals the fact that ammonium more closely resembles rubidium than it does potassium.

*Rubidium magnesium phosphate*, $RbMgPO_4 + 6H_2O$, separates immediately on adding a warm solution of magnesium chloride to a mixture of rubidium chloride and disodium phosphate dissolved in water, the amorphous precipitate rapidly becoming crystalline; it is decomposed by silver nitrate, but resists the action of boiling water.

*Hydrogen rubidium magnesium carbonate*, $HRbMg(CO_3)_2 + 4H_2O$, is obtained by saturating an aqueous solution of rubidium carbonate with carbonic anhydride, and heating the liquid with magnesium carbonate during 5 minutes at 60°, a current of carbonic anhydride being passed through the liquid meanwhile; the filtered liquid deposits minute, transparent rhombs, having the edges flattened. The salt effloresces in a few days when exposed to air, and in this respect resembles hydrogen ammonium magnesium carbonate, whilst the potassium salt may be preserved for years without undergoing change.

*Lead rubidium chloride*, $PbRb_2Cl_6$, is obtained under the conditions observed by Friedrich, in preparing the analogous ammonium salt (Abstr., 1893, ii, 415); it is a yellow, crystalline powder, which closely resembles lead ammonium chloride. Concentrated sulphuric acid acts on it, liberating hydrogen chloride, and precipitating lead tetrachloride as an oil (compare *loc. cit.*), whilst the dilute acid converts the metals into sulphates, and liberates chlorine. Rubidium chloride may be precipitated almost quantitatively from its solution in methylic alcohol saturated with chlorine by adding a solution of lead tetrachloride, the precipitate being washed with 80 per cent. alcohol. Lead potassium chloride is much less stable than the rubidium salt, and evolves chlorine when dried in the air; the same change takes place when the rubidium salt is heated, the tetrachloride, $PbRb_2Cl_4$, being produced. The rubidium salt is also indifferent towards dilute hydrochloric acid and 96 per cent. alcohol, the potassium salt being decomposed by both agents; the changes produced under the influence of water and ammonia are less rapid than those which the potassium salt undergoes. In spite of these differences in behaviour, the estimation of rubidium in presence of potassium by means of lead tetrachloride is inaccurate; this agent, however, may be employed for the production of purified rubidium chloride from a solution containing 2 per cent. of potassium chloride.

Rubidium salts also resemble ammonium salts in respect to their volatility, and it is not possible to remove ammonium chloride from rubidium chloride by application of heat, without loss of the rubidium salt. Traube has shown that the atomic solution volume of rubidium is equal to that of ammonium (Abstr., 1895, ii, 70). M. O. F.

**Electrolytic Silver Peroxide.** By OTTOKAR ŠULC (*Zeit. anorg. Chem.*, 1896, **12**, 180—181).—The author points out that the product

of the electrolysis of silver nitrate which he recently described (Abstr., 1896, ii, 521), and to which the formula $Ag_7NO_{11}$ was ascribed, may be regarded as a compound of silver peroxide and the heptoxide of nitrogen, and as being of the composition $7Ag_2O_2,N_2O_7$. The properties of the compound are consistent with this formula. H. C.

**Peroxides in their Relationship to the Periodic System of the Elements.** By AUGUSTO PICCINI (*Zeit. anorg. Chem.*, 1896, **12**, 169—179).—The author considers peroxides of the hydrogen peroxide type, such as $BaO_2$, $TiO_3$, and $S_2O_7$, in their relationship to the periodic system and to the question of the type of the highest oxygen compounds. As a general characteristic of oxides of this class may be quoted their reduction in acid solution by such oxidising agents as $MnO_2$, $PbO_2$, and $KMnO_4$. This distinguishes the peroxides from all other classes of oxides, and the peroxides are also distinguished by their lack of the acidic character that usually attaches to the higher oxides. These and other marked differences between the peroxides and the ordinary oxides of the water type lead to the conclusion that the peroxides cannot be regarded as compounds typical of the highest combining powers of the elements. H. C.

**Double Bromides.** By RAOUL VARET (*Compt. rend.*, 1896, **123**, 497—500).—The author has measured the heat developed on mixing aqueous solutions of mercuric bromide and of other metallic bromides capable of forming double salts of the type $2HgBr_2,MBr_2,nH_2O$, or $HgBr_2,MBr_2,nH_2O$, experiments being made with solutions of different degrees of concentration. As a rule, the development of heat is greater the more concentrated the solutions, and it is also increased by the presence of an excess of the soluble bromide. Similar experiments were made with cobalt and manganese bromides, and sodium and ammonium bromides.

The heats of formation in solution of the compounds of mercuric bromide with other metallic bromides are of the same order of magnitude for a given series of double salts, any differences that are observed being due to the unequal thermal effects resulting from dilution in different cases. The results lead to the conclusion that these double salts are derived from complex acids, such as $H_2Hg_2Br_6$ and $H_2HgBr_4$. The double salts formed by cobalt or manganese bromide with sodium or ammonium bromide are dissociated to a large extent on dialysis, and the thermal effects produced by mixing dilute solutions of their proximate constituents are very slight. C. H. B.

**Aluminium Amalgam.** By VICTOR BIERNACKI (*Ann. Phys. Chem.*, 1896, [2], **59**, 664—667).—A rod or wire of aluminium can be readily amalgamated by connecting it with one pole of a battery the other pole of which is connected with mercury, and then dipping the aluminium into the mercury and removing it again several times. The sparks formed each time at the connecting surfaces serve to heat the aluminium sufficiently to induce combination with the mercury. As the mercury in the amalgam appears to play the part of a catalytic agent, the smallest quantity of mercury at the end of an aluminium

wire will bring about oxidation of very considerable amounts of aluminium. H. C.

**The Constitution of Inorganic Compounds.** By ALFRED WERNER and ARTURO MIOLATI (*Zeit. physikal. Chem.*, 1896, **21**, 225—238).—The authors determined the electrical conductivity of various ammoniacal cobalt compounds with a view to the elucidation of their constitution. The conductivity of Jörgensen's dinitrotriaminecobalt chloride (Abstr., 1895, ii, 48) increased with the time, reaching a final constant value consistent with the presence of a univalent cation. The chlorine is, therefore, not present originally in the ion state, and hence cannot be united to the amine group, as Jörgensen supposed. The trinitrotriamine compound, $Co(NH_3)_3(NO_2)_3$, also contains no ion, the value for the conductivity being very low—1·6 at $v = 1000$, and totally different from that of the croceocobaltic nitrite,

$$NO_2\cdot Co(NO_2)_2(NH_3)_4;$$

$\mu = 90$ at $v = 1024$. The nitritochlorotetraminecobalt chloride,

$$Cl\cdot Co\{NO_2Cl(NH_3)_4\},$$

originally gave the value $\mu = 68$ ($v = 240$), but after remaining for 70 minutes at 0°, the value had increased to 104, this being due probably to hydrolysis into $Co\{NO_2H_2O(NH_3)_4\}Cl_2$. The praseo-salts appear to undergo an analogous hydrolysis, from $Co\{(NH_3)_4Cl_2\}Br$ into $Co\{(NH_3)_4(H_2O)_2\}Cl_2Br$, as the conductivity increased in 40 minutes, from 116·6 to 332·1 with a final maximum = 372 ($v = 512$), the nitrite and nitrate exhibiting similar changes. The hydrogen sulphate, however, only gave an increase of from 373 to 439 ($v = 256$) so that, in this case, the final compound appears to be $Co\{(NH_3)_4H_2OCl\}SO_4$, the conductivity of which in 1/256 HCl solution is 439·7. The diaquodichlorodiamine salts, $Co\{(NH_3)_2(H_2O)_2Cl_2\}Cl$, also gave a marked increase after a time, corresponding with the ionisation of the two chlorine atoms. The sulphato-pentamine compounds contain the complex ion,

$$Co(NH_3)_5SO_4,$$

whilst a rapid increase of conductivity by dilution indicated hydrolysis to $Co(NH_3)_5H_2O$. The chloropentamine, aquopentamine, and aquochlorotetramine salts were also examined, and, as in the previous cases, the results indicated hydrolysis to aquo-salts, and were in complete accord with the author's views of the constitution of these compounds. (Abstr., 1894, ii, 407.) L. M. J.

**Nickel Dioxide and its Acid Properties: Barium Nickelite.** By EM. DUFAU (*Compt. rend.*, 1896, **123**, 495—497).—When an intimate mixture of nickelic oxide (85 parts) with barium oxide (155 parts) or barium carbonate (200 parts) is surrounded by barium oxide and heated for 10 minutes in the electric furnace with an arc from 60 volts and 300 ampères, a fused, grey mass is obtained with a crystalline fracture. It soon disintegrates when exposed to the air, and when rapidly treated with cold water, levigated, and finally washed and levigated with alcohol, it yields small, brilliant, dark-coloured crystals, which

are greenish-brown when powdered; sp. gr. = 4·8 at 20°; hardness a little above 4.

The crystals consist of barium dinickelite, $BaO,2NiO_2$, and are somewhat unstable. Cold water attacks them slowly and hot water rapidly. Hydrofluoric acid dissolves them with effervescence, and hydrochloric acid, with evolution of chlorine; nitric acid and ammonia, also dissolve and decompose them. Chlorine, bromine, and iodine attack the nickelite at a red heat, with formation of halogen salts of the metals, but oxygen has no action at bright redness. Sulphur, a little above its melting point, converts the nickelite into sulphides, with incandescence. Hydrogen fluoride and hydrogen chloride decompose it at a red heat, but fused neutral oxidising agents are without action on it.

It follows from these observations that nickel dioxide not only exists but has acid properties analogous to those of cobalt and manganese dioxides. Since nickelic oxide has no acid properties, it is probable that the oxide $Ni_3O_4$ has the constitution $NiO_2,2NiO$. C. H. B.

**Diffusion of Sulphides through Steel.** By EDWARD D. CAMPBELL (*Amer. Chem. J.*, 1896, **18**, 707—719).—Ferrous sulphide, cuprous sulphide, nickel sulphide ($Ni_4S_3$), and the product obtained by melting together ferrous sulphide and iron (? subsulphide of iron) are incapable of diffusing through steel bars heated to bright redness. When a mixture of 400 grams of ferrous sulphide with 13 per cent. of its weight of magnetic oxide of iron was melted, a product was obtained which the author regards as impure oxysulphide of iron, $Fe_2OS$; this was found to diffuse readily through red-hot steel bars and to have the property when mixed with cuprous sulphide, of carrying this with it. It is suggested that $Fe_2OS$, being at the temperature of the experiments an extremely mobile liquid (as shown by its rapid passage through the walls of the clay crucible used in its preparation), is able to diffuse through the steel on account of the porosity of the latter substance at a bright red heat. A. C. C.

**Influence of Heat Treatment and of Carbon on the Solubility of Phosphorus in Steels.** By EDWARD D. CAMPBELL and S. C. BABCOCK (*Amer. Chem. J.*, 1896, **18**, 719—723).—The authors have investigated the influence of the percentage of carbon in steel, and of the slow or sudden cooling of the latter on the solubility of the contained phosphorus. Estimations were made of the percentages of phosphorus (*a*) soluble in a neutral solution of mercuric chloride, (*b*) insoluble in mercuric chloride but soluble in 4 per cent. hydrochloric acid, and (*c*) insoluble in either of the above two liquids, and the following conclusions are arrived at:—(1) With very low carbon percentages, the rate of cooling of the metal has but little effect on the solubility of the phosphorus; (2) with increase of carbon, hardening diminishes the solubility, and (3) with high carbon percentages the solubility of the phosphorus is increased by slow cooling. It is suggested that these results point to the probable formation at a high temperature of a difficultly soluble compound of iron with carbon and phosphorus, which passes on slow cooling into an easily soluble one. A. C. C.

**Bismuth Oxyiodide.** By T. R. BLYTH (*Chem. News*, 1896, **74**, 200).—The residue from the distillation of the double iodide of methylamine and bismuth with caustic soda, and the product of boiling bismuth oxyiodide, BiOI, with the same reagent, both have a composition corresponding with the formula $Bi_{17}I_3O_{24} = BiI_3,8Bi_2O_3 = 3BiOI,7Bi_2O_3$. It is a light, microscopically crystalline powder, with a very slight brown tint, soluble in dilute hydrochloric acid, not attacked by boiling water or alkalis, but is decomposed by nitric acid with liberation of iodine and by hydrogen sulphide with formation of sulphide. D. A. L.

---

## Mineralogical Chemistry.

**Advances in Mineralogical Chemistry.** By BERNARD J. HARRINGTON (*Trans. Roy. Soc., Canada*, 1895, [2], 1, Sect. III, 3—17).—A presidential address, dealing generally with the separation, analysis, synthesis, and constitution of minerals. L. J. S.

**Selenium associated with Gold and Bismuth: Graphitic Slate, and Water from N.S. Wales.** By J. MILNE CURRAN (*J. and Proc. Roy. Soc., N.S.W.*, 1895, **29**, 404—408).—A slate from Mount Hope, N.S.W., containing native gold with bismuth oxide and carbonate, gave reactions for selenium; no sulphides were detected, but originally there was probably present an auriferous selenide or sulphide of bismuth.

A lustrous graphitic slate from Yalcogrin, on analysis, showed 12·5 per cent. of graphite.

The granite of the Wyalong gold-field is decomposed to a depth of 150 to 190 feet; the water supply from this decomposed rock gave, in grains per gallon: $SiO_2$, 37·268; $Al_2O_3$, 3·052; CaO, 43·540; MgO, 109·144; $Na_2O$, 551·236; $K_2O$, 6·188; $SO_3$, 192·430; Cl, 924·784; water of crystallisation, 209·300; Zn, trace; total (less O for Cl), 1868·55. Large quantities of soluble organic matter are present. Considering the origin of the water, there is a large amount of sodium chloride in it.

Some trachytes and other rocks from New South Wales are described. L. J. S.

**Two New Mineral Substances from Broken Hill, N.S.W.** By EDWARD F. PITTMAN (*J. and Proc. Roy. Soc., N.S.W.*, 1895, **29**, 48—51).—These substances, from the Australian Broken Hill Consols mine, are different from anything hitherto described, but they are only alteration products and mineral mixtures.

One of them is an alteration product of dyscrasite, which mineral it sometimes envelops; it is massive, and in sections shows a finely banded structure; the colour is greyish-brown, and the mineral is

sectile; the sp. gr. of one specimen is 4·9. Analysis by J. C. H. Mingaye gave the results under I, by H. P. White those under II.

| | Moisture at 100°. | Comb. $H_2O$. | Ag. | Sb. | Cu. | Pb. | As. | Au. | CaO. |
|---|---|---|---|---|---|---|---|---|---|
| I. | 0·56 | 4·04 | 47·46 | 16·87 | 0·11 | 0·62 | trace | trace | 3·78 |
| II. | 0·13 | 4·37 | 45·87 | 20·72 | 0·48 | 0·31 | trace | — | 4·25 |

| | MgO. | $Fe_2O_3$. | Cl. | Insol. | O [diff.]. |
|---|---|---|---|---|---|
| I. | 1·17 | 2·11 | 13·69 | 1·01 | [8·58] |
| II. | 0·20 | 0·45 | 12·27 | 0·90 | [10·05] |

The silver exists as chloride and antimonide; the former is nearly all dissolved out from the powdered mineral by strong ammonia solution, leaving a residue which gave the following results on analysis:—

| Ag. | Au. | Sb. | As. | Pb. | Cu. | Fe. | Ca. | Mg. |
|---|---|---|---|---|---|---|---|---|
| 19·71 | trace | 35·12 | trace | 2·79 | 0·52 | 5·18 | 4·84 | 0·17 |

| Insol. | Cl. | $H_2O$. | O. | Total. |
|---|---|---|---|---|
| 5·20 | 0·14 | 6·01 | 19·69 | 99·37 |

The second substance is an alteration product of argentiferous galena; it is dark grey, has a cubical structure, and is sectile; the sp. gr. of one specimen is 6·38. The following analyses by Mingaye and White show that the composition is very variable.

| | Moisture. | $Ag_2S$. | $Cu_2S$. | $FeS_2$. | $PbSO_4$. | PbS. | Insol. | Total. |
|---|---|---|---|---|---|---|---|---|
| I. | 0·08 | 77·99 | 0·62 | 1·42 | 19·36 | — | 0·30 | 99·77 |
| II. | — | 76·62 | 0·32 | 0·45 | 19·80 | 0·50 | 1·60 | 99·73 |
| III. | 0·14 | 13·25 | 1·82 | 0·42 | 77·60 | 2·20 | 4·50 | 99·93 |
| IV. | — | 10·86 | 2·00 | — | 84·61 | 0·96 | 1·00 | 99·93 |

In II is also 0·44 per cent. of $Sb_2S_3$, and in IV 0·50 per cent. of $Fe_2O_3$. Ammonium acetate dissolves lead sulphate from the polished surface, leaving the silver sulphide in relief. L. J. S.

[Antimony Ochre, Celestite, Galena, Graphite, Tetrahedrite, Meymacite and Anthraxolite from Canada.] By G. CHRISTIAN HOFFMANN (*Ann. Report* (1894) *Geol. Survey, Canada*, 1896, N.S., 7, R., 1—68).—*Antimony ochre* occurs as an earthy incrustation, of a wine-yellow colour, on the stibnite of South Ham, Wolfe Co., Quebec. Analysis gave

| $Sb_2O_4$. | $As_2O_3$. | $Fe_2O_3$. | $Al_2O_3$. | CaO. | MgO. | $H_2O$. | Quartz. | Total. |
|---|---|---|---|---|---|---|---|---|
| 58·86 | 7·88 | 2·82 | 1·02 | 5·71 | 0·61 | 9·46 | 13·39 | 99·75 |

*Celestite* occurs, sometimes with calcite and galena, as a vein in crystalline limestone at Lansdowne, Leeds Co., Ontario; it is colourless, yellowish, or bluish, and semitransparent. Analysis shows it to be nearly pure strontium sulphate.

| $SO_3$. | SrO. | BaO. | CaO. | Total. | Sp. gr |
|---|---|---|---|---|---|
| 43·51 | 56·31 | trace | 0·11 | 99·93 | 3·958 |

*Galena* containing free sulphur, from West Kootanie, British Columbia, forms a coarsely crystalline aggregate with bright cleavage surfaces, and showing no visible signs of alteration. It readily takes fire, and burns with a pale blue flame. From the powdered mineral, carbon

bisulphide extracts sulphur, and ammonium acetate extracts lead sulphate. The mean of two very similar analyses is

| S (free). | S (comb.). | $SO_4$. | Pb. | Sb. | Fe. | Zn. | Ag. | Total. |
|---|---|---|---|---|---|---|---|---|
| 3·95 | 7·48 | 12·61 | 72·19 | 0·85 | 0·29 | 1·08 | 0·72 | 99·17. |

This amount of $SO_4$ corresponds with 39·81 per cent. $PbSO_4$.

*Graphite*, from Marmora, Hastings Co., Ontario, is very finely granular, with uneven fracture, greyish black colour and dull lustre. It contains 72·13 per cent. of apparently amorphous graphite. The ash contains $SiO_2$, 36·0; $Al_2O_3$, 32·8; $Fe_2O_3$, 11·2; CaO, 2·0; MgO, 7·6 per cent.

*Plumbiferous tetrahedrite*, massive, with indistinct fibrous structure, from West Kootanie, British Columbia, gave the following results on analysis; sp. gr. 5·082.

| S. | Sb. | As. | Cu. | Ag. | Pb. | Zn. | Fe. | Quartz. | Total. |
|---|---|---|---|---|---|---|---|---|---|
| 20·59 | 26·81 | 0·22 | 21·03 | 10·64 | 8·91 | 5·91 | 0·88 | 5·57 | 100·56. |

*Meymacite* occurs as a dull to bright yellow ochre with the scheelite of Marlow, Beauce Co., Quebec; it is a tungsten oxide with 7·2 per cent. of water. All the above analyses are by R. A. A. Johnston.

*Anthraxolite*, from a quartz vein in limestone and bituminous shale at Lake Petitsikapau, Ungava district, Labrador Peninsula, has an irregular structure, and is intermixed with quartz and other fragments; it gave on analysis

| $H_2O$ at 110—115°. | Loss on ignition in a closed vessel. | Fixed C. | Ash. | Total. |
|---|---|---|---|---|
| 3·56 | 2·48 | 86·83 | 7·13 | 100·00. |

The ash consists mainly of silica; another specimen gave 0·31 per cent. ash.

Various other mineralogical notes, chiefly relating to occurrences, are given. The report also includes analyses of coals, iron ores, nickeliferous pyrrhotite, calcareous marls, and waters, as well as the results of numerous gold and silver assays. L. J. S.

**Bauxite and Emery.** By A. Liebrich (*Zeit. prakt. Geol.*, 1895, 275—277).—It is pointed out that bauxite occurs in the younger rocks, whilst emery occurs in the oldest (gneisses, &c.); and that in their chemical composition the only important differences are the much larger amount of water in bauxite, and the presence of ferrous oxide (in the magnetite) in emery. Analyses of bauxite, calculated without the water, compare very closely with analyses of emery. This similarity of composition suggests that the two minerals may have the same origin; bauxite has been derived from silicates by decomposition, and the same must be true for emery, which has been brought into the present state by the action of water under pressure and at a high temperature. L. J. S.

**Greenockite from Laurion.** By Anastasios C. Christomanos (*Tsch. Min. Mitth.*, 1896, **16**, 360—361; and *Compt. rend.*, **123**, 62). —The calamine of Laurion, Attica, is very varied in colour and struc-

ture; a reddish, amber-yellow variety, which is vitreous and translucent, gave the following results on analysis.

| ZnO. | CdO. | FeO. | CaO. | MgO. | $Al_2O_3$. | $SiO_2$. | S. | $CO_2$. | Total. |
|---|---|---|---|---|---|---|---|---|---|
| 62·060 | 2·700 | 0·592 | 0·123 | 0·219 | 0·020 | 0·180 | 0·190 | 33·895 | 99·979 |

This corresponds with 92·57 per cent., $ZnCO_3$, 2·07 ZnO, 2·62 $CdCO_3$, and 0·85 CdS. Dusted over the surface, and in cavities, is a bright yellow, amorphous powder; the following analysis shows this to be greenockite.

| Cd. | S. | Zn. | $CO_2$. |
|---|---|---|---|
| 77·22 | 22·47 | trace | trace |

L. J. S.

**Origin of Malachite.** By EDGAR HALL (*J. and Proc. Roy. Soc., N.S.W.*, 1895, **29**, 416—419).—In an abandoned mine, in which the ore is cupriferous pyrites, the author has found malachite and azurite, and copper and iron sulphates; as the malachite and copper sulphate are both sometimes fibrous, it is suggested that the former is pseudomorphous after the latter. In dry seasons, the decomposition of the ore would give rise to an efflorescence of sulphates, which in wet seasons would be altered to carbonates by the action of carbonate solutions. L. J. S.

**Blue Apatite from Montebras.** By ADOLPHE CARNOT (*Bull. Soc. fran. Min.*, 1896, **19**, 214—215). In the tin mine of Montebras, Creuse, a darkish violet-blue apatite occurs in a very micaceous granite. With the cassiterite of this locality are several other phosphates, namely, amblygonite, montebrasite, wavellite, turquoise, and phosphates of iron and manganese. The apatite, on analysis, gave

| $P_2O_5$. | F. | Cl. | CaO. | MgO. | MnO. | $Fe_2O_3$. | Quartz. | Total. |
|---|---|---|---|---|---|---|---|---|
| 39·60 | 3·23 | trace | 50·45 | trace | 1·22 | 0·20 | 6·35 | 101·05 |

This corresponds with :—

| $Ca_3P_2O_8$. | $Mn_3P_2O_8$. | $FePO_4$. | $CaF_2$. | Quartz. | Total. |
|---|---|---|---|---|---|
| 84·30 | 2·03 | 0·38 | 6·62 | 6·35 | 99·69 |

The colour appears to be due to the manganese, which exists, for the most part, as manganous phosphate. L. J. S.

**"Mangankiesel" from the Harz.** By FRIEDRICH KLOCKMANN (*Jahrb. k. Preuss. geol. Landesanst. u. Bergakad.*, 1895 (1894), **15**, p. xxxii).—In a quartz-schist on the Steinbergkappe, in the Western or Upper Harz, is a band, 1 foot thick, of compact, reddish-white to grey "mangankiesel"; analysis by Erbrich gave

| MnO. | CaO. | MgO. | $CO_2$. | $SiO_2$. | Undeter. | Total. |
|---|---|---|---|---|---|---|
| 32·251 | 0·477 | 0·910 | 18·097 | 49·009 | 0·756 | 101·500 |

This occurrence is very similar to that at Schebenholz, near Elbingerode. L. J. S.

**The Genesis of the Talc Deposits of St. Lawrence Co., N.Y.** By CHARLES H. SMYTH, jun. (*School of Mines Quart.*, 1896, **17**,

333—341).—In the gneissic area of the Adirondacks are large belts of crystalline limestones which often contain tremolite and enstatite; these minerals sometimes predominate, and the limestones graduate into tremolite and enstatite schists. Intimately associated with these schists, and, in fact, graduating into them, are the talc deposits. The talc, being pseudomorphous after these fibrous minerals, is itself fibrous in structure, this structure being parallel to the cleavage of the original mineral. For a very soft specimen, apparently derived from enstatite, the optic axial angle was determined as 56° 36′, and for a slightly harder piece, 80° 34′; these values are much greater than is usual for talc, and they evidently decrease with the progress of alteration of the original mineral. With this fibrous talc ("agalite") is also a little of the more usual form of foliated talc in soft, pearly scales; this is almost optically uniaxial, and, unlike the former, is not pseudomorphous in origin but of independent growth. The alterations would have been effected by circulating water containing carbonic acid, probably under pressure, as shown by the equations

$$\underset{\text{Enstatite.}}{4MgSiO_3} + H_2O + CO_2 = \underset{\text{Talc.}}{H_2Mg_3Si_4O_{12}} + MgCO_3$$

$$\underset{\text{Tremolite.}}{CaMg_3Si_4O_{12}} + H_2O + CO_2 = \underset{\text{Talc.}}{H_2Mg_3Si_4O_{12}} + CaCO_3.$$

This substitution of $H_2$ for Ca is in agreement with Clarke's acid metasilicate formula for talc. The resulting carbonates would be carried away by the excess of carbonic acid. These talc deposits have, then, been derived from tremolite and enstatite schists, which, in turn, have originated by the metamorphism of a siliceous magnesium limestone poor in alumina. L. J. S.

**Minerals of the Gross-Venediger in the Hohe Tauern.** By ERNST WEINSCHENK (*Zeits. Kryst. Min.*, 1896, **26**, 337—508).—The Gross-Venediger of the Austrian Alps consists of a central mass of granite surrounded by eclogites, amphibolites, gneisses, schists, phyllites, &c., these containing isolated patches of serpentine. The secondary mineral veins occurring in these rocks are of two distinct types. One is of general distribution, and is characterised by the presence of a little titanic acid; the minerals of constant occurrence are quartz, felspar, apatite and calcite, whilst the other minerals depend on the kind of rock containing the veins. The other type of veins occurs in connection with the serpentines, and is of local distribution; here quartz and felspar are absent, and the surrounding rocks have no influence on the mineral contents of the veins.

Detailed descriptions are given of 60 mineral species found in the district, and analyses are given of the following:—I, Pistachio-green epidote, occurring with magnetite and diopside in an epidote-rock in connection with the serpentine. II, Red garnet. III, Massive garnet, from a garnet-chlorite-rock, which is an alteration product of serpentine; the crystals of II rest on this massive garnet, and the two are very similar in appearance, but differ in composition. IV, Hyacinth-red garnet from an epidote-idocrase-rock. V, Clove-brown garnet from a rock containing epidote, diopside and magnetite. VI, Hyacinth-

red garnet. VII, Brown garnet. The above analyses of garnet, with the exception of III, by Muthmann, are quoted from H. Schnerr (*Inaug.-Diss., Munich*, 1894). VIII, Acicular diopside from crevices in a hornblende-schist. IX, Light green diopside. X, Albite from crevices in amphibolite and eclogite; it contains also $Na_2O$, 11·19; $K_2O$, 0·19 per cent.

| | $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | CaO. | FeO. | MnO. | MgO. | $H_2O$ or loss on ignition. |
|---|---|---|---|---|---|---|---|---|
| I. | 38·15 | 23·51 | 14·32 | 23·41 | 0·18 | — | — | 1·93 |
| II. | 36·33 | 7·35 | 21·64 | 32·36 | 1·91 | 0·48 | — | 0·29 |
| III. | 38·32 | 17·38 | 7·56 | 31·72 | 2·49 | 1·50 | 0·48 | 0·71 |
| IV. | 37·53 | 11·99 | 14·79 | 33·55 | 1·68 | 0·28 | — | 0·48 |
| V. | 35·97 | 7·07 | 22·51 | 31·51 | 2·88 | trace | — | 0·25 |
| VI. | 37·96 | 16·29 | 8·73 | 31·98 | 4·46 | 0·57 | — | — |
| VII. | 36·56 | 7·44 | 20·94 | 23·59 | 1·17 | trace | — | — |
| VIII. | 52·08 | 1·96 | — | 23·31 | 9·21 | 0·35 | 12·75 | — |
| IX. | 54·19 | 0·07 | — | 22·76 | 2·05 | 0·43 | 20·24 | — |
| X. | 67·76 | 20·15 | — | 0·77 | — | — | — | — |

L. J. S.

**Disintegration and Decomposition of Diabase.** By GEORGE P. MERRILL (*Bull. Geol. Soc. Amer.*, 1896, 7, 349—362).—The diabase of a large dyke at Medford, Massachusetts, has been extensively disintegrated to a reddish-brown, sandy material. The fresh rock is quite firm, but contains some calcite, a little zeolite and chlorite, and shows a slight kaolinisation of the felspars. Under I, is the bulk analysis of the fresh diabase, and under II, that of the portion soluble in hydrochloric acid and sodium carbonate solution (1·19 per cent. of the silica being soluble in the former). Under III, is that the bulk analysis of the disintegrated rock, and IV, is that of the soluble portion (0·85 per cent. of the silica being here soluble in hydrochloric acid). These analyses show that the disintegration is accompanied by decomposition and a leaching out of the more soluble constituents. As would be expected, more of the fresh rock is soluble in acid and alkaline solutions than of the altered rock. Analysis V, is of the fine silt and clay, which forms only 3·17 per cent. of the altered rock. 78·87 per cent. of it is soluble in hydrochloric acid and sodium carbonate, and under the microscope the material shows felspar and other silicates.

| | I | II | III | IV | V | VI | VII |
|---|---|---|---|---|---|---|---|
| $SiO_2$ | 47·28 | 10·85 | 44·44 | 9·50 | 36·61 | 8·48 | 18·03 |
| $Al_2O_3$ | 20·22 | 4·74 | 23·19 | 4·86 | } 40·68 | } 0·00 | 0·00 |
| $Fe_2O_3$ | 3·66 | } 10·91 | 12·70 | 10·00 | | } 2·42 | 18·10 |
| FeO | 8·89 | | | | | | |
| CaO | 7·09 | 3·09 | 6·03 | 1·50 | 3·44 | 1·83 | 25·89 |
| MgO | 3·17 | 2·20 | 2·82 | 1·84 | 4·02 | 0·68 | 21·70 |
| MnO | 0·77 | n.d. | 0·52 | n.d. | n.d. | 0·32 | 41·57 |
| $K_2O$ | 2·16 | 1·21 | 1·75 | 0·68 | 1·82 | 0·62 | 29·15 |
| $Na_2O$ | 3·94 | 0·50 | 3·93 | 0·17 | 2·14 | 0·50 | 12·83 |
| $P_2O_5$ | 0·68 | n.d. | 0·70 | n.d. | — | 0·08 | 11·39 |
| Ignition | 2·73 | 2·73 | 3·73 | 3·73 | 10·97 | 0·53 | 0·00 |
| Total | 100·59 | 36·23 | 99·81 | 32·28 | 99·68 | 14·93 | — |

Column VI gives the percentage loss for the entire rock, as calculated from I and III, on the supposition that the total amount of alumina has remained unaffected during the alteration of the rock, and column VII gives the percentage loss of each constituent, as calculated from I and VI. Calculating the results on this basis brings out points which are not obvious on mere inspection of the bulk analyses of the fresh and altered rock; for example, it is seen that calcium, potassium, iron and magnesium have been relatively largely removed. The analyses of the granite of the district of Columbia (Abstr., 1896, ii., 483) are here recalculated in this manner. The assumption that the total amount of alumina remains constant is taken from Roth, but it does not always seem to be correct, for in some cases ferric oxide is more refractory than the alumina.

The relative rapidity of rock weathering in high and low latitudes is discussed, and it is insisted that the rapid disintegration in warm, moist climates has been emphasised too much. Here, decomposition follows more closely upon disintegration, whilst in cold regions, where the action of frost is a potent factor, disintegration exceeds decomposition. The term degeneration, to include both disintegration and decomposition, is proposed. L. J. S.

**Dust which fell [in Austria-Hungary] in February, 1896.** By Conrad H. von John (*Verh. k.k. geol. Reichsanst.*, 1896, 259—264). —On February 25th. and 26th., 1896, there was a fall of dust and snow over a large area in Hungary, mainly about the Platten See, but extending into Austria as far north as Austrian Silesia. The dust from different localities is very similar, being dark brown, and of extreme fineness. Under the microscope, the principal constituent is seen as grains of a grey, transparent, amorphous material, which analysis shows to be a clay. There are also black particles of organic matter, numerous grains and splinters of quartz, and a few fragments of augite, zircon, rutile, etc. Mica and remains of organisms were not found. The first four of the following analyses are of material from different localities. All contain a little carbonic acid and organic matter. The first contains 2·92 and the second 2·48 per cent. of carbon.

| $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | CaO. | MgO. | $K_2O$. | $Na_2O$. | $H_2O$ (at 100°). | Loss on ignition. | Total. |
|---|---|---|---|---|---|---|---|---|---|
| 49·29 | 15·50 | 6·17 | 4·23 | 2·46 | 2·94 | 1·02 | 2·80 | 16·09 | 100·50 |
| 52·25 | 13·95 | 7·10 | 3·85 | 2·45 | 3·05 | 1·46 | 2·78 | 12·96 | 99·85 |
| 52·50 | 14·20 | 6·40 | 3·80 | 2·45 | 2·97 | 1·44 | 3·02 | 13·80 | 100·58 |
| 55·28 | 15·24 | 6·58 | 3·66 | 2·63 | [2·57] | | 3·01 | 11·03 | 100·00 |
| 45·10 | 15·95 | 13·25 | 4·85 | 2·64 | 1·95 | 0·85 | 6·70 | 8·84 | 100·47 |

The great similarity shown in these analyses points to a common origin for the dust. The decrease in silica to the north is explained by quartz having fallen before the other constituents. The last of the above analyses is of Nile mud (containing also 0·34 $SO_3$, 1 per cent. C, and some $CO_2$), and it is suggested that the dust in question came from Egypt; as, however, there was no storm at Alexandria from 21st. to 26th. of February, it may have come from Servia and S. Hungary.

L. J. S.

**The Arlington Iron.** By NEWTON H. WINCHELL (*Amer. Geologist*, 1896, 18, 267—271).—This iron was found in March, 1894, at $2\frac{1}{2}$ miles north-east of Arlington, Sibley Co., Minnesota. It is roughly heart-shaped, with an average thickness of 1 inch; weight $19\frac{3}{4}$ lbs. The convex side is tolerably smooth and has a spotted appearance, whilst the opposite, nearly plane, surface is pitted and rough, some of the pits almost penetrating the specimen. Three structural directions, brought out by etching, are described in detail. Analysis by F. F. Sharpless gave:

| Fe. | Ni. | Co. | P. | Total. |
|---|---|---|---|---|
| 90·781 | 8·605 | 1·023 | 0·045 | 100·454 |

Also Cr, Cu, and combined carbon in traces; S, Si, and Mn are absent. The composition does not appear to be uniform, as four determinations of the iron varied between 90·58 and 91·74; the carbon also varies. L. J. S.

**Discovery of Argon in the Gases of a Spring at Perchtoldsdorf, near Vienna.** By MAX BAMBERGER (*Monatsh.*, 1896, 17, 604—612). The gas from the same spring was investigated in 1853 by Ragsky, who showed that the gas contains 93·8 per cent. of nitrogen. The author confirms Ragsky's analyses, but, also finds that the gas described as nitrogen by Ragsky contains 1·11—1·24 per cent. of argon. J. J. S.

**Water from a Mineral Spring in Mitchell Co., Kansas.** By EDGAR H. S. BAILEY and MARY A. RICE (*Trans. Kansas Acad. Sci.*, 1896 (1893—4), 14, 40—41).—Water from a spring 2 miles east of Cawker City and half a mile south-east of the celebrated "Great Spirit Spring," in Mitchell Co., Kansas, gave in parts per 100,000: $SiO_2$ and insoluble matter, 1·53; $Fe_2O_3$ and $Al_2O_3$, 1·66; CaO, 38·66; MgO, 61·48; $SO_3$, 269·50; $K_2O$, 21·20; $Na_2O$, 753·30; Cl, 740·00; $B_2O_3$, trace; $CO_2$ (calculated), 35·69. This composition is very similar to that of the water of the "Great Spirit Spring." L. J. S.

**Thermal Spring at Wiesbaden.** By C. REMIGIUS FRESENIUS and ERNST HINTZ (*Jahrb. Nassau. Ver.*, 1896, *Jahrg.* 49, 3—23).—The water of the Augusta Victoria bath at Wiesbaden has a temperature of 40°; sp. gr. = 1·006455 at 14°. Analysis gave, in parts per 1000: NaCl, 6·644452; KCl, 0·172013; LiCl, 0·018825; $NH_4Cl$ 0·012666; $CaCl_2$, 0·599187; NaBr, 0·004920; NaI, 0·000025; $CaSO_4$' 0·068816; $SrSO_4$, 0·024678; $BaSO_4$, 0·001381; $CaH_2(CO_3)_2$, 0·364834, $MgH_2(CO_3)_2$, 0·248852; $FeH_2(CO_3)_2$, 0·001392; $MnH_2(CO_3)_2$, 0·001716; $Ca_2As_2O_7$, 0·000045; $Ca_3P_2O_8$, 0·000081; $CaB_2O_4$, 0·002565; $SiO_2$,; 0·059782; free $CO_2$, 0·282091; total, 8·508321. Also traces of rubidium, cæsium, nitric acid, titanic acid, copper, and organic substances. This composition is very similar to that of other thermal waters of Wiesbaden containing sodium chloride; analyses of these are quoted for comparison. Full analytical details are given in the paper. L. J. S.

**Carbonated Water from Seifersdorf (Austrian Silesia).** By ERNST LUDWIG (*Tsch. Min. Mitth.*, 1896, **16**, 133—139).—Water from a spring at the village of Seifersdorf, in Austrian Silesia, gave, in 10,000 parts: $K_2SO_4$, 0·057; $Na_2SO_4$, 0·037; NaCl, 0·058; $Na_2CO_3$, 1·775; $CaCO_3$, 7·171; $SrCO_3$, 0·021; $MgCO_3$, 1·000; $FeCO_3$, 0·179; $MnCO_3$, 0·026; $Al_2O_3$, 0·001; $SiO_2$, 0·620; organic matter, 0·040; $CO_2$ in bicarbonates, 4·499; $CO_2$ free, 17·449; total solids, 10·985; also traces of lithium and phosphoric acid. Sp. gr. = 1·00163 at 17·2° (compared with distilled water at the same temperature). The composition of the water remains constant throughout the course of the year, and the temperature only varies from 10—12°. The rocks of the district are limestones, clayey sandstones, and also some of volcanic origin. L. J. S.

**The Constantin-Spring in Gleichenberg (Styria).** By ERNST LUDWIG (*Tsch. Min. Mitth.*, 1896, **16**, 140—149).—The celebrated mineral waters of Gleichenberg, Styria, were known to the Romans; analyses of the water of the Constantin-spring have previously been made by Schrötter (1834) and Gottlieb (1864). The results of the present analysis are, in parts per 10,000: $K_2SO_4$, 1·023; KCl, 0·012; NaCl, 18·223; $Na_2B_4O_7$, 0·082; $Na_2HPO_4$, 0·006; $Na_2CO_3$, 25·060; $Li_2CO_3$, 0·039; $CaCO_3$, 3·541; $SrCO_3$, 0·054; $BaCO_3$, 0·004; $MgCO_3$, 4·215; $FeCO_3$, 0·027; $MnCO_3$, 0·002; $Al_2O_3$, 0·002; $SiO_2$, 0·647; organic matter, 0·054; $CO_2$ in bicarbonates, 14·212; $CO_2$ free, 20·519; total solids, 52·937; also traces of cæsium and rubidium. These results agree, in the important constituents, with the older analyses, so that there has been no change in the composition of the water during the last 60 years. Sp. gr. = 1·0057 at 17·6° (compared with distilled water at the same temperature). The temperature of the water is 17·3°. The rocks of the district are mainly trachytes, together with basalts and Tertiary sands and marls. From the water, opal has been deposited in the trachyte, and pebbles and plants have been cemented together by a siliceous deposit. L. J. S.

**Deposit from a Chalybeate Water.** By E. C. CASE (*Trans. Kansas Acad. Sci.*, 1896 (1893—4), **14**, 36—37).—Water from a well near Lawrence, and close to the bank of the Kansas River, gave, in parts per 100,000: $SiO_2$ and insoluble matter, 4·50; $Fe_2O_3$ and $Al_2O_3$, 3·45; $CaSO_4$, 9·31; $CaCO_3$, 15·03; $MgCO_3$, 6·72; NaCl, 14·43; total solids, 53·44; $CO_2$ (free and in bicarbonates), 25·01. The water is at first clear, but, on standing, soon becomes turbid. In the well is a homogeneous deposit having the following composition, which approaches that of limonite: $SiO_2$ and insoluble matter, 19·30; $Fe_2O_3$ with a little $Al_2O_3$, 46·95; $H_2O$ below 100°, 9·15; $H_2O$ at 230°, 14·40; $CaSO_4$, 0·25; $CaCO_3$, 7·32; $MgCO_3$, 0·75; NaCl, 0·60 per cent.; organic matter, not determined. From this it is seen that the silica has remained in solution to a larger extent than the iron. The well is sunk in gravel containing nodules of limonite, and this has been dissolved by the percolating carbonated water; the iron in the freshly-drawn water exists in the ferrous state. L. J. S.

# Physiological Chemistry.

**Absorption of Dextrose in the Small Intestine, and the Effects of Drugs on the Process.** By FRIEDRICH VON SCANZONI (*Zeit. Biol.*, 1896, 33, 462—474).—Ethereal oils, oil of mustard, alcohol, pepper, and orexin have, in certain concentrations, a favourable influence on the absorption of dextrose in the intestine, as in the stomach. In the stomach, the absorption may be increased fivefold, but this is not nearly so well marked in the intestine; the rise is only a few degrees per cent., for the intestine is already, in normal circumstances, the ideal place for dextrose absorption. The dose necessary to stimulate the intestine is smaller; for instance, oil of mustard (1 in 200) has no harmful effect on the stomach and stimulates the absorption process there, but it is harmful to the intestine.

W. D. H.

**Absorption of Peptone in the Small Intestine, and the Effect of Drugs on the Process.** By ERNST FARNSTEINER (*Zeit. Biol.*, 1896, 33, 475—488).—A 1 per cent. aqueous solution of peptone was introduced through a fistula into the ileum in a dog, and after 15 minutes, 63 per cent., on the average, was absorbed.

Addition of 5 per cent. alcohol raised this figure to 72—74; oil of mustard (1 : 1500—5000) to 72—73; oil of cinnamon (1 : 500) to 69. The effect of these drugs is not so marked as in the stomach. Bitters like quassia have no constant action. Mucilages hinder absorption; 2 per cent. of starch brings the absorption down to 21—25 per cent.

W. D. H.

**Changes in Cane Sugar in the Alimentary Canal.** By HEINRICH KÖBNER (*Zeit. Biol*, 1896, 33, 404—407).—Inversion of cane sugar does not occur in the stomach, nor in artificial gastric digestion. The statement often made to the contrary is owing (1) to dextrose being present from the remains of the previous meal; (2) to the ingestion of sugar which had previously been partly inverted; and (3) to the fact that in pathological cases, especially if there is a transudation of serum into the stomach, inversion may occur.

Inversion begins in the small intestine; cane sugar is, however, resistant, and may be found in small amounts quite low down the intestine. Absorption of cane sugar occurs most rapidly in the stomach and duodenum.

W. D. H.

**Iron in the Animal Organism.** By WINFIELD S. HALL (*Chem. Centr.*, 1896, i, 970; from Du Bois Reymond's *Archiv*, 1896, 49—83).—Carniferrin was added to food free from iron, and given to white mice; the tissues being examined microchemically by the ammonium sulphide method, and control experiments made on mice that had had no carniferrin. The whole animals were also incinerated, and the iron estimated in the ash. In those fed only on food free from iron, there was

a loss of 40 per cent. in the total iron of the body in three weeks. In those fed on carniferrin, the red corpuscles increased in number, and absorption of the iron was found to occur chiefly in the duodenum, and to a less extent in the jejunum. Storage of iron occurred in the spleen, and to a less extent in the liver. The liver, large intestine, and kidney appear also to excrete iron. W. D. H.

**The Value of Rhamnose in the Normal and Diabetic Organism.** By LUDWIG LINDEMANN and RICHARD MAY (*Chem. Centr.*, 1896, i, 932—933 from *Deutsch. Arch. Klin. Med.*, **56**, 283—294).—In a healthy man, about 8 per cent. of the rhamnose given was recovered in the urine; in a diabetic patient, 11·7 per cent. in the urine and 4·4 per cent. in the fæces was recovered; there was a simultaneous excretion of dextrose, but the nitrogenous output was diminished from 17 to 14·8 grams per diem. Rhamnose acts, therefore, as a proteid-sparing food. W. D. H.

**The Proteids of Leucæmic Urine.** By RUDOLF KOLISCH and RICHARD BURIÁN (*Chem. Centr.*, 1896, i, 972—973, from *Zeits. Klin. Med.*, **29**, 374—380).—Albumosuria is not a constant feature in leucæmia; when present, it probably originates from the decomposition of leucocytes, the increase in alloxuric substances in the urine supporting this view. The principal new point made out in the case described is the occurrence of Lilienfeld's histon in the urine.

W. D. H.

**Luciferase, or the Light-producing Enzyme of Animals and Plants.** By RAPHAEL DUBOIS (*Compt. Rend.*, 1896, **123**, 653—654).—The author is of opinion that the active agent in the production of light by certain animals and plants is a substance having the general characters of an enzyme, to which he therefore gives the name *luciferase*, and that it is not the result of slow oxidation. The luminiferous organs of the glow-worm, and the eggs contained in the ovaries of the female, give with tincture of guaiacum, a fine, blue coloration, as does also the luminous mucus from the surface of dead fish after treatment with chloroform water and filtration. A. C. C.

**Analyses of Human, Cows', and Mares' Milk.** By WILLIAM CAMERER and FRIEDRICH SÖLDNER (*Zeit. Biol.*, 1896, **33**, 535—568. Compare Abstr., 1896, ii, 378).—A very large number of analyses of human, cows', and mares' milk are given; in the case of human milk, the different dates of lactation are stated. The paper is chiefly composed of tables of results, which cannot be conveniently shortened, and do not appear to show any new points of interest.

W. D. H.

**Constancy of the Freezing Points of Milk and other Organic Liquids.** By J. WINTER (*Bull. Soc. Chem.*, 1896, [3], **15**, 162—163).—The author finds that his observations (Abstr., 1896, ii, 199) have been to some extent anticipated by Beckmann.

**Excretion of Calcium in Diabetes.** By ERNST TENBAUM (*Zeit. Biol.*, 1896, **33**, 379—403).—The increased amount, both of liquid and solid nutriment taken by diabetics, accounts, in large measure, for the increase in the volume of urine and amount of nitrogen excreted. When such increase occurs, the quantity of calcium salts in the urine increases also in a proportionate way. The large output of calcium appears to be dependent solely on the increased nutriment taken. Calcium and proteid are so closely associated that this is what would be expected. W. D. H.

## Chemistry of Vegetable Physiology and Agriculture.

**The Changes which take place in Milk, either Spontaneously, or during Culinary Processes.** By ANTOINE BÉCHAMP (*Bull. Soc. Chim.*, 1896, [3], 15, 96).—An historical sketch of the development of the germ theory of fermentation of organic solutions. M. W. T.

**Putrefaction of Albumin.** By OSKAR EMMERLING (*Ber.*, 1896, **29**, 2721—2726).—In these experiments, pure proteids were treated with pure cultivations of micro-organisms.

I. Behaviour of wheat gluten with *Proteus vulgaris*. Wheat paste freed from starch by treatment with malt and repeated washing with water, and from fatty substances by washing with alcohol and ether, was mixed with calcium carbonate, potassium phosphate, and magnesium sulphate, and placed in the Koch steam steriliser for 3 days, it was then mixed with the *Proteus* and kept in an incubator at 37°; after 4 days, gas began to be evolved, which consisted of 46 per cent. $CO_2$, 38 per cent. H, and 16 per cent. N. After 14 days, the process was stopped, and the strongly alkaline liquid distilled in a current of steam. *The distillate* consisted of phenols and volatile bases, from which trimethylamine was isolated and identified. *The residue* contained the non-volatile bases, and the acids as their calcium salts; in the former, betaine was present, and was isolated by means of its aurochloride (m. p. 227°). The acids were separated by the fractional precipitation of their silver salts, formic, acetic, and butyric acids being identified.

II. Behaviour of Egg albumin with *Staphylococcus pyogenes aureus*. The decomposition products, isolated in the same way, were found to be, in *the distillate*, phenol, indole, and scatole, and in *the residue, volatile*, formic, acetic, propionic, butyric, and traces of higher fatty acids; *non-volatile*, oxalic and succinic acids. Betaine and trimethylamine were also present. J. F. T.

**A New Bacillus which forms Butyric Acid from Glycerol.** By OSKAR EMMERLING (*Ber.*, 1896, **29**, 2726—2727).—This bacillus, for which the author proposes the name *Bacillus boocopricus*, is isolated from cow-excrement by Fritz's method. It is very similar to *B. subtilis*, and grows well on gelatin. With beef broth, it does not form indole. With glycerol, at 36°, in the presence of calcium

carbonate, methylic alcohol, acetic acid, butyric acid, and traces of formic and succinic acids are produced; 6 grams of alcohol, 4·5 grams of acetic acid, and 7 grams of normal butyric acid being obtained from 600 grams of glycerol. From grape sugar, ethylic alcohol and lactic acid are produced. J. F. T.

**The Cause of Poisoning by Curtains containing Arsenic.** By OSKAR EMMERLING (*Ber.*, 1896, **29**, 2728).—As the result of a large number of experiments conducted with different bacilli and micrococci, the author states that in no case is hydrogen arsenide evolved from fabrics containing arsenic by their means. It is, therefore, highly improbable that poisoning from woollen stuffs containing arsenic is due to hydrogen arsenide, evolved by the action of a micro-organism.

J. F. T.

**Denitrifying Bacteria and the Loss of Nitrogen caused by them.** By R. BURRI and ALBERT STUTZER (*Ann Agron.*, 1896, **22**, 491—494; from *Centr. Bact. Par.*, 1895, 1, 2 Abt., 257, 350, 392 and 422).—From horse-dung, two bacteria were isolated, which together, but not singly, decomposed nitrites with liberation of free nitrogen. The one was identified as *Bacterium coli commune*, whilst the other is new, and is designated *B. denitrificans I.* Another variety, *B. denitrificans II.*, which alone liberates nitrogen from nitrates and nitrites, was isolated from old straw. This micro-organism throve in artificial solutions as well as in nitrate-broth, and destroyed the nitrate in the same length of time. *B. coli* with *B. denit. I.*, however, caused no turbidity in the artificial solution in a week, and did not decompose the nitrate in the least, in absence of complex nitrogen compounds.

The destruction of nitrates (in both) is checked when the amount of nitrate present exceeds 0·5—0·6 per cent. This holds both for *B. coli* with *B. denit. I.* and for *B. denit. II.* This has nothing to do with the production of nitrite (which is not poisonous, as the author formerly supposed), but to excessive alkalinity.

In the presence of 0·06—0·07 per cent. of phosphoric acid the fermentation produced by *B. coli* with *B. denit. I.* was checked, whilst *B. denit. II.* remained active in presence of 0·14 per cent. of phosphoric acid.

Quantitative experiments with *B. denit. II.* in artificial solutions, showed that 22·2, 20·3 and 20·6 per cent. of the nitrogen of the nitrates remains, and is probably in the form of proteids. On one occasion, 79·5, on another 82·7, per cent. was evolved as gas. Neither carbonic anhydride nor nitrous oxide could be detected.

In the complete absence of oxygen, *B. denit. I.* with *B. coli* reduce nitrates completely, but without evolution of nitrogen, the nitrate being almost entirely converted into nitrite. With very limited access of air, *B. denit. I.* will develop sufficiently to give rise (in conjunction with *B. coli*) to evolution of free nitrogen; whilst with abundant aëration the evolution of nitrogen is normal.

*B. denit. II.* decomposes nitrates normally in complete absence of air, whilst with aëration, the fermentation is hindered or completely stopped. N. H. J. M.

**Origin of Trimethylamine, and the Spontaneous Development of Heat in Hops.** By JOHANNES BEHRENS (*Bied. Centr.*, 1896, **25**, 713—714; from *Der Bierbrauer*, 1896, 578—579).—Whilst, according to Griesmayer and Greshoff, trimethylamine is a constituent of hops, the author was unable to detect its presence either in fresh hops, or in hops which had been kept in the dry state. In presence of water, however, hops acquire a very repulsive odour, in which that of trimethylamine can readily be detected. This change, and the rise of temperature which accompanies it, is due to a bacterium (*Bacillus lupuliperda*) which resembles Flügge's *B. fluorescens putibus* both morphologically and physiologically. The nitrogenous substances of the hops which are utilised by the bacillus are proteids, choline, ammonia, and asparagine, whilst malic and citric acids, &c., supply carbon. The tannin present in the hops does not seem to be changed by the bacillus. The antiseptic nature of hops prevents the development of other micro-organisms. N. H. J. M.

**Action of Phenylquinolines and Phosphines on Lower Organisms.** By A. J. F. HERMANN TAPPEINER (*Chem. Centr.*, 1896, i, 1010—1011; from *Deutsch. Arch. Klin. Med.*, **56**, 369—380).—Those organisms (Infusoria, Amœbæ, Turbellaridæ) on which quinine works strongly are even more readily killed by phenylquinolines and phosphines; those (yeasts, bacteria) on which quinine has but little action are less affected by the compounds in question. Of the phenylquinolines, the $\beta$-compound acts most strongly, the $\alpha$-compound least so.

W. D. H.

**Vegetation in Respired Air.** By LOUIS MANGIN (*Bied. Centr.*, 1896, **25**, 689—690; from *Jour. Agric. prat.*, 1896, i, 491—493).—Equal quantities of seeds and tubers were placed, with equal amounts of water, in each of a series of receivers through which air was drawn by means of a pump. The apparatus was so constructed that a small quantity of air could be withdrawn for analysis. As the air became richer in carbonic anhydride and poorer in oxygen, growth was considerably retarded. Whilst linseed absorbed 3·29 per cent. of oxygen, and produced 1·44 per cent. of carbonic anhydride in an atmosphere containing 1 to 3 per cent. of carbonic anhydride, the amounts were 1·45 and 1·04 per cent. when 2 to 5 per cent. of carbonic anhydride was present. In the case of peas, the amount of substance produced diminished from 53·5 to 42·5 grams when the percentage of carbonic anhydride rose from 1—3 to 2—5 per cent. There was, moreover, a change in the nature of the oxidation process indicated by an increase in the quotients $CO_2/O_2$. With linseed, for instance, this was 0·51 in an atmosphere containing 1—3 per cent. of carbonic anhydride, and 0·74 when the percentage was 2—5 N. H. J. M.

**Production of Vegetable Proteids.** By TAMÁS KOSUTÁNY (*Landw.-Versuchs.-Stat.*, 1896, **48**, 13—32). The object of the author's experiments was to throw light on the question whether assimilation, and the process of reduction which it involves, influences the production of proteids from asparagine. Assuming that amides are formed

from proteids as secondary products of oxidation in germinating seeds, it seemed likely that, in developed plants, proteids might be formed from amides in the process of deoxidation under the influence of light.

Comparative experiments were made in which the one half of a number of leaves of *Riparia sauvage* were cut during the day (between 2 and 3 p.m.), the remaining halves being separated from the plants in the night, and analysed.

The percentage of total nitrogen diminished as the season advanced. In the 1894 experiments, the difference was about 0·25 per cent. (from 21st June to the end of August), but in 1895, with a longer interval, the percentage diminished from 5·314 (on May 8) to 1·25 at the end of October. As regards variations in composition during day and night, the total nitrogen was somewhat higher during the night than in the day time (102·37 : 100), but the non-proteid nitrogen is much less by night than by day (45 : 100). The leaves contain rather more ammonia but less nitric acid in the night than in the day time. Since, in the night, oxidation prevails in the plant, it is probable that the conversion of nitrates into proteids is greatest in the night. No asparagine, or similar substance, could be detected in the leaves cut off in the night. It is concluded that, whilst the crude substances which produce proteids are chiefly taken up by the plant in the day time, their actual conversion into proteids takes place more in the night than in the day.

The leaves contain on the average 1·10 per cent. more water in the night than in the day time. Leaves cut in the day time contain the most sugar, those cut in the night the most free acids.

The percentage of ash increased, somewhat irregularly, from 9·43 on May 8 to 19·93 on October 23. N. H. J. M.

**Effect of Nitrogen on Root Formation.** By HERMANN MÜLLER (*Bied. Centr.*, 1896, **25**, 595—597; from *Jahresber. Versuchs-stat. Wädensweil.*, 1895, **4**, 48).—Water-culture experiments were made in which half of the roots of a number of plants were immersed in nutritive solutions free from nitrogen, the other half in solutions containing nitrogen. The plants selected were vetches, maize, sunflower, and beans, &c. In presence of nitrogen, the root-development was greatly increased. It is concluded that proteids are formed in the roots, and not in the leaves only; otherwise, it must be assumed that the proteids migrated to the roots directly supplied with nitrogen, and not to those (of the same plants) growing in solutions free from nitrogen. N. H. J. M.

**The Physiological Significance of Lecithin in Plants.** By JULIUS STOKLASA (*Ber.*, 1896, **29**, 2761—2771).—The important part which is played by phosphoric acid in plant physiology has led the author to determine the proportion of lecithin occurring in certain vegetable organs; the paper forms a summary of the analytical results and the conclusions which they suggest. Seeds which are rich in albumin contain also a greater proportion of lecithin, whilst oily seeds, those, for instance, of *Brassica oleracea*, *Sinapis arvensis*, and *Beta vulgaris*, are poor in lecithin; germination of the last-named is not accompanied by decomposition of lecithin, but in the case of *Pisum*

*sativum* this process involves reduction in the percentage of the substance in question. In the fruit of maize, 74 per cent. of the total quantity of lecithin is found in the embryo and scutellum, only 26 per cent. occurring in the endosperm; from this fact, the author concludes that the lecithin in the scutellum, and especially in the embryo, under the influence of radiant energy, serves to elaborate chlorophyll in the early stages of plant life. Development of the leaf is also associated with the production of lecithin, which increases with the multiplication of chlorophyll granules; this increase is in some way related to the assimilation of carbonic anhydride, and it appears probable to the author that lecithin arises in the granules themselves as a product of assimilation. Moreover, analyses show that vine leaves, when allowed to grow for 10 days in darkness, contain only one-third as much lecithin as similar, but unprotected, leaves from the same plant collected at the same time of day (4 o'clock).

*Chlorolecithin** is an amorphous, greenish-black substance with metallic lustre, which has been isolated from freshly-gathered, unpressed grass leaves; its behaviour towards baryta indicates the presence of choline, glycerylphosphoric acid, and chlorophyllan groups, and, in this respect, it resembles Hoppe-Seyler's chlorophyllan, differing from that substance, however, in the amount of phosphorus present, for whilst chlorophyllan contains only 1·38 per cent., chlorolecithin contains 3·37 per cent.

Thus the author has traced an intimate connection between lecithin and chlorophyll, and maintains that, not only does the former substance actually occur in chlorophyll granules, but that phosphorus is a constituent of chlorophyll, and that without this element the elaboration of chlorophyll and the development of chlorophyll granules is impossible.

Examination of apple-blossom has shown that the pedicel is engaged in transmitting lecithin from the leaf to the flower. The petals are richest in lecithin previous to fertilisation, acting as storage vessels, which become rapidly depleted of lecithin when the fruit is formed. The pollen contains 6 per cent. of lecithin, and, Zacharias having shown that nucleïn occurs in this product, it is noteworthy that animal spermatozoa also contain lecithin and nucleïn. M. O. F.

**Coexistence of Laccase and Tyrosinase in certain Fungi.** By GABRIEL BERTRAND (*Compt. rend.*, 1896, **123**, 463—465).—An extract of various species of *Russula* obtained by plasmolysis with washed chloroform or ether, has much more active oxidising properties than extracts prepared by the methods previously described. It also acts on tyrosin, in addition to having the oxidising properties of laccase, and it would seem that both ferments are present in the extract. This is confirmed by the fact that, when the extract is heated at 70°, the power of affecting tyrosin disappears, whilst the extract still attacks the substances that are oxidised by laccase. When an extract of *Russula delica* in aqueous chloroform is mixed with excess of alcohol, a precipitate is formed, and the liquid does not attack tyrosin, but oxidises phenols and amines in the same manner as laccase. The precipitate, when purified by suspension in chloroform and reprecipitation by alcohol, yields

* This is not a chlorinated derivative of lecithin, as its name would seem to imply —[EDITORS].

an aqueous solution which has practically no action on phenols and amines, but rapidly oxidises tyrosin. It follows that laccase and tyrosinase coexist in the juice of many species of fungi (compare Abstr., 1896, ii, 61, 268, 571).

C. H. B.

**Nitrogenous Constituents of Beet-Juice.** By EDMUND O. VON LIPPMANN (*Ber.*, 1896, **29**, 2645—2654).—Of the nitrogenous compounds present in beet-juice, the following have been already obtained and more or less carefully characterised: asparagine, glutamine, betaïne and choline, leucine and tyrosine, glutamic or pyroglutamic acid, citrazinic acid, lecithin, and legumin.

The author has already pointed out (Abstr., 1888, and *Zeit. f. Rubenzuck. Ind.*, **38**, 68) that, besides lecithin, the cell-substance contains other phosphorus compounds, which may be extracted by means of alkalis, and are probably closely related to the nucleïns, and, further, that their decomposition products, the xanthine-compounds, may be obtained from the molasses by fractional precipitation with phosphotungstic acid. He has now succeeded in isolating a considerable number of nitrogenous substances in the following manner.

The dilute solution of the decomposition products was neutralised and precipitated with lead acetate, phosphotungstic acid, or mercuric nitrate, and the precipitates formed were then decomposed, in order to liberate the contained bases, which were subsequently fractionally precipitated by means of phosphotungstic acid, mercuric nitrate, mercuric chloride, &c.

The following substances were isolated and completely characterised: xanthine, guanine, hypoxanthine, adenine, carnine (rarely observed in plants), arginine, guanidine, allantoïn, and possibly vicin. The investigation is complicated by the occurrence of the decomposition products of these substances.

The recurrence of vicin, a glucoside, in the above product of alkaline hydrolysis is not impossible, as would at first sight appear, as Drenkmann has described a glucoside (*Zeit. f. Rubenzuck. Ind.*, **46**, 478) which is only slowly decomposed by strong alkali at high temperatures.

A. L.

**The Maximum of Plant Production.** By ADOLF MAYER (*Landw. Versuchs.-Stat.*, 1896, **48**, 61—76).—The maximum production of the various agricultural plants, as grown in ordinary agricultural practice, was previously shown (*ibid.*, 1892, **40**, 205) to be 7000—8000 kilos. per hectare in Northern Europe, although by very heavy manuring twice that amount, or more, could be obtained.

With regard to the question whether the limit of production depends on the amount of sunlight or on the amount of carbonic anhydride in the air, the results of Dehérain's experiments on sugar beet (Abstr., 1890, 406), in which a greater yield was obtained under the influence of farmyard manure, as compared with minerals, seem to point to the production of carbonic anhydride from the organic manure as the cause of the increased yield, especially as the soil to which minerals were applied was shown to be poor in carbonic anhydride. (Dehérain attributed the greater yield on the dung-plot to the direct assimilation of organic matter.) In 1893 and 1894, the author made experiments with sugar beet (on plots of 0·25 are) in which plants received (1) farmyard manure

(120,000 kilograms per hectare), (2) minerals, and (3) minerals in conjunction with carbonic anhydride (liberated on the spot from 10 per cent. dextrose solution and yeast). The results indicated that the highest yield of sugar beet can be obtained with exclusively mineral manure, when sufficiently watered, as well as with farmyard manure. It is not possible to explain Dehérain's results, as the plan of the experiments is not fully given; but it seems likely that the beneficial effect of the farmyard manure must, at any rate, be largely due to the increased water-capacity of the soil. N. H. J. M.

**Nutritive Value of Horse-chestnuts.** By PAUL GAY (*Ann. Agron.*, 1896, **22**, 401—423).—The horse-chestnuts employed in the experiments had the following percentage composition.

| Water. | Crude proteïn. | Ether extract. | N-free extract. | Crude cellulose. | Ash. |
|---|---|---|---|---|---|
| 38·93 | 4·81 | 4·64 | 46·19 | 3·66 | 1·77 |

Two lots of sheep were fed with lucerne (500 grams), peas (500 grams), with the addition of mangolds and horse-chestnuts respectively, given in such quantity that the amount of dry matter of each was the same. The increase of live weight was much greater in the case of the sheep fed with chestnuts than with those fed with roots. On reversing the foods, the same result was again obtained. It is concluded that raw chestnuts are about three times as nutritive as mangolds. The value of chestnuts is considerably increased by cooking. In experiments with cows, in which 5 kilos. of chestnuts per head per day were given, it was found that no effect was produced either on the taste or composition of the milk, and the milk had no injurious effect on calves. The yield of milk was, however, considerably diminished (from 15 to 12 kilos. per day). This is ascribed to deficiency of water in the food, in which case the remedy would be easy.

Pigs declined to eat chestnuts in any quantity, and left more than half the food with which they were mixed. N. H. J. M.

**Molasses as Food for Cows.** By AUGUST STELLWAAG (*Bied. Centr.*, 1896, **25**, 718—719; from *Zeit. landw. Ver. Bayern*, 1895, 778). —Four cows were fed for a week with chaff (two-thirds hay and one-third straw, 20 kilos.), fresh brewers' grains (20 kilos.), malt germs (2 kilos.), and crushed barley (4 kilos. per 1000 kilos. live weight). For two of the cows, the same feeding was continued four weeks longer; whilst the other two, instead of the barley, had molasses mixed with an equal weight of palm cake (3 kilos.). During the next four weeks, the food of the two sets of cows was reversed. The composition of the molasses food resembled that of the barley, but contained somewhat less carbohydrates and rather more fat. The cows consumed the whole of the molasses mixture (which was mixed with the brewers' grains), and did not suffer from indigestion. There was no change, either in the amount of milk or in the percentage of fat, during the experiments.

N. H. J. M.

**Recent Progress in Soil Examination.** By EUGENE W. HILGARD (*Rep. Agric. Exper. Stat. Univ. Cal. for* 1894—5, 23—32).—A number of Californian and Hawaiian soils were analysed, employing Dyer's

citric acid extraction method, and the results obtained agreed exceedingly well with vegetation experiments.

With regard to the recognition of "nitrogen hunger" in soils, the author recommends separation and analysis of the humus. The more nitrogenous the humus is, the less carbon will be oxidised by the limited amount of oxygen present in the soil. It was previously concluded that a soil in which the humus contained less than 2·5 per cent. of nitrogen would be benefited by nitrogenous manure, notwithstanding that the soil itself contained as much as 0·17 per cent. of nitrogen. This opinion was confirmed by a vegetation experiment, which clearly showed that available nitrogen was deficient. The amount of lime present in the soil is, however, of great importance in this connection. With a deficiency of lime, soils would show "nitrogen hunger," even when the humus contained more than 2·5 per cent. of nitrogen, whilst in calcareous soil, a low percentage of nitrogen might suffice.

The author thinks that the examination of humus, in conjunction with Dyer's method for mineral constituents, will eventually furnish a means of readily ascertaining the wants of soils, although the vegetation tests (in pots or in the field) will have the last word. N. H. J. M.

**Behaviour of Superphosphate and Basic Slag in Soil.** By St. Smorawski and H. Jacobson (*Bied. Centr.*, 1896, **25**, 580—581; from *Blätter f. Zuckerrübenbau*, 1896, **3**, 193—201).—Basic slag and mineral and bone superphosphates respectively (about 1 per cent.) were mixed with soil, and the phosphoric acid soluble in water and in citrate solution was determined. The soil was then put into beakers, moistened with water, and left to dry, being occasionally stirred. The phosphoric acid was again determined as before. This was repeated several times at intervals of 4 to 8 weeks.

The results indicate that the phosphoric acid originally soluble in water is very rapidly converted into the citrate-soluble form, but this has no effect on its value as manure. The citrate-soluble phosphate seems to undergo no further change. The alleged inferiority of basic slag is, therefore, unfounded.

Mineral and bone superphosphates containing the same percentage of phosphoric acid have equal value as manures. N. H. J. M.

**Assimilability of Nitric and Ammoniacal Nitrogen by Plants.** By Aimé Pagnoul (*Ann. Agron.*, 1896, **22**, 485—490).—Mangolds, *Camelina*, clover, and oats were grown in sterilised sand, (1) without any manure, (2) with sodium phosphate and potassium nitrate, and (3) with sodium phosphate, potassium chloride, and ammonium sulphate; as compared with nitrate, ammonium sulphate gave two or three times as much dry produce in each case. The unmanured plants were quite free from nitrates. The plants which received nitrate contained 0·35 to 0·75 per cent. of nitrogen as nitrates (in the dry substance), whilst those which received ammonium sulphate contained much less, but still quite appreciable amounts (0·017 to 0·150 per cent.). Nitrogen in the form of ammonia was found in the plants manured both with nitrate and with ammonium sulphate, but in much smaller quantity than nitric nitrogen. The results indicate that, under the

conditions of the experiments, nitrogen was directly assimilated in the form of ammonia, and in greater quantity than in the form of nitrates.

Nitrogen as nitrates was determined in the plants as follows: After drying the substance at 105°, a small quantity (0·2 gram) was boiled with a little water, and, when cold, treated with a few drops of lead acetate solution, and about a gram of animal charcoal. After an hour, it was filtered and diluted to 50 c.c.; of this solution, 5 c.c. was evaporated to dryness, well stirred with a few drops of phenol dissolved in sulphuric acid (1 : 7), and treated with ammonia. The yellow colour thus produced, if nitrates were present, was compared with that of a standard solution of ammonium picrate (N = 1 per million), by pouring the two solutions into two similar tubes, each holding 50 c.c. and divided into c.c. The solution to be tested is diluted until it has the same tint as 50 c.c. of the standard solution, and its volume $V$ (in c.c.) read. The amount of nitrogen in milligrams per cent. =

$$\frac{V \cdot 10000}{2000} = 5V.$$

Ammonia was determined by distilling the fresh substance (10 grams) with water (50 c.c.), magnesia (0·5 gram), paraffin (0·5 gram), and a few pieces of pumice, using a spiral condenser; the distillate, which is collected in a flask containing a few drops of very dilute sulphuric acid, is diluted to 50 c.c. and treated with Nessler solution, employing, for comparison, a solution of ammonium sulphate (N = 1 per million). N. H. J. M.

**The Agricultural Value of Deteriorated Phosphatic Manures.** By JULES JOFFRE (*Bull. Soc. Chim.*, 1896, [3], 15, 42—46).—Millot has proved that the deterioration of phosphatic manures is due to the formation of an insoluble ferric phosphate. To determine the relative values of superphosphate, tricalcium phosphate, and the ferric phosphate obtained from a sample of manure containing very little tricalcium phosphate, from which all the soluble phosphate had been removed, crops of mustard were grown in plots which differed only with regard to the nature of the phosphate present.

The results were as follows.

| | |
|---|---|
| Plot without fertiliser | 100 |
| Plot with ferric phosphate from deteriorated superphosphate | 167 |
| Plot with tricalcium phosphate | 280 |
| Plot with superphosphate | 360 |

M. W. T.

## Analytical Chemistry.

**Methods of Rock Analysis.** By MAX DITTRICH (*Mitth. Badisch. geol. Landesanst.*, 1894, 3, 75—105).—The methods are essentially those usually adopted, the material being first fused with sodium and potassium carbonates; several small variations are described in detail. L. J. S.

**Estimation of the Three Halogens, Chlorine, Bromine, and Iodine, in Mixtures of their Binary Compounds.** By A. A. BENNETT and L. A. PLACEWAY (*J. Amer. Chem. Soc.*, 1896, **18**, 688—692). —Two grams of the mixed salts is dissolved in 150 c.c. of water; 50 c.c. of a 20 per cent. solution of iron alum is added, and the iodine is expelled by distillation; this, as usual, is condensed in an apparatus containing 35 c.c. of 20 per cent. potassium iodide and titrated.

The bromine is then liberated by adding 35 c.c. of a saturated solution of potassium permanganate and distilling, in the usual way, into potassium iodide solution, when it sets free an equivalent quantity of iodine.

After reducing the excess of permanganate with sulphuric acid and ferrous sulphate, the chlorine is precipitated with silver nitrate.

L. DE K.

**Action of Bromine on Metallic Chlorides and a Method for the Estimation of both Halogens in the presence of one another.** By FRITZ BLAU (*Monatsh.*, 1896, **17**, 547—566).—The author has taken the experimental numbers obtained by Berthelot (Abstr., 1881, 342; 1883, 8; 1885, 632) in his experiments on the amount of chlorine liberated by the action of bromine on different chlorides, and from these has calculated the affinity constant $K$ by means of the equation $K^2 = \frac{(A-C)\ (B-C)}{C^2}$ where $A$ = the number of equivalents of chloride originally present, $B$ = those of bromine, and $C$ = the (necessarily equal) number of equivalents of bromide and chlorine produced in the reaction. The results thus obtained are roughly of the same magnitude, and differ completely from those based on Humpidge's data (Abstr., 1884, 1245). This divergence can probably be accounted for by the inaptitude of the indirect method for the estimation of chlorine and bromine when one of these is present in a large excess. The author has carried out experiments on the action of bromine on concentrated sodium chloride solutions. In making the experiments, a measured quantity of a solution of pure sodium chloride was placed in a stoppered flask, and a weighed quantity of pure bromine, contained in a small, thin-walled bulb, dropped in; on shaking, the bulb was broken, and the flask was placed in the dark at a constant temperature for several hours. The excess of bromine and the liberated chlorine were then quickly removed by a rapid current of air which had been filtered through cotton wool, and as soon as the last trace of bromine was thus removed, the amounts of sodium bromide and chloride in the solution were estimated. Exact analytical results were obtained by using a modification of Berglund's method (Abstr., 1885, 836) for the estimation of bromide and chloride in the presence of one another. For this purpose, the bromine was set free by means of potassium permanganate and potassium hydrogen sulphate; and the solution distilled in a vacuum at the ordinary temperature in a special apparatus, the bromine being collected in aqueous potash. The hypobromite thus formed was converted into bromide, and the liquid treated exactly as before, the bromine in the second distillate being estimated by means of iodine. The residues in the two distillation flasks were united, and the amount of chloride contained in them estimated.

The author finds that at 12—13° $K = 272{\cdot}67$, and at 16—17° $K = 246{\cdot}08$.

Care was taken to show that no secondary actions took place, as the solution formed was quite neutral. It was also proved experimentally that the current of air always removed the two halogens in the same proportion, so that the equilibrium was not disturbed.

J. J. S.

**Jacobsen and Brunn's Method for the Purification by means of Iodine of Hydrogen Sulphide containing Arsenic.** By Zdenko H. Skraup (*Chem. Centr.*, 1896, i, 469; from *Zeit. Österr. Apoth.-V.* **34**, 72—76).—In testing the efficiency of this method (Jacobsen, Abstr., 1887, 885), which is based on the facts that hydrogen arsenide and dry iodine form arsenic tri-iodide, whilst hydrogen sulphide and iodine do not react in the absence of water, the gas, after washing with water and subsequent drying by means of calcium chloride, was passed over dry iodine, then into sodium hydroxide solution (?) and then into warm nitric acid. The residue obtained on evaporating the nitric acid was treated with sulphuric acid and submitted to Marsh's test. Slow passage of the gas through the apparatus was found to effect either a complete removal of arsenic or to leave only slight traces, but unsatisfactory results were obtained when a more rapid current was employed.

E. W. W.

**Estimation of Sulphur in Pyrites.** By Georg Lunge (*J. Amer. Chem. Soc.*, 1896, **18**, 685—686).—A final reply to Gladding (Abstr., 1895, ii, 291, and 1896, ii, 622). Experiments conducted on behalf of the author have again shown that, when precipitating a sulphate with barium chloride solution, the latter may be added either quickly and in moderate excess, or run in from a burette at the rate of one drop per second without any sensible difference in the result.

L. de K.

**Estimation of Sulphides in Calcium Carbide.** By Frederick J. Pope (*J. Amer. Chem. Soc.*, 1896, **18**, 740—741).—A weighed quantity of the sample is introduced into a dry Erlenmeyer flask provided with a stop-cock funnel and a delivery tube leading to a 10 oz. wash-bottle, which is in turn connected with a smaller one; both are partially filled with a standard solution of lead acetate, the total value of which is, of course, accurately known. The calcium carbide is first decomposed by water until no more acetylene is evolved, and excess of dilute sulphuric acid is then introduced and the mixture boiled; hydrogen sulphide is evolved, and precipitates part of the lead as sulphide. The excess of lead is then estimated by the author's method (this vol., ii, 125).

L. de K.

**Estimation of Sulphur in Ores.** By J. H. Stansbie (*Chem. News*, 1896, **74**, 189). Lucien L. de Koninck (*ibid.*, 224).—Stansbie suggests the use of nitric acid and bromine for the oxidation of sulphur in ores, whilst de Koninck points to a similar application of the same reagents by himself years ago.

D. A. L.

**Estimation of Sulphuric Acid or of Barium.** By James Edmunds (*Chem. News*, 1896, **74**, 187—188).—For the proposed method, there

are required decinormal and centinormal solutions of barium nitrate, potassium chromate, silver nitrate, sodium chloride, and potassium sulphate, centinormal solutions of potassium thiocyanate and calcium sulphate, and a decinormal solution of ferric sulphate. The latter is made by oxidising a solution of ferrous sulphate by boiling with nitric acid, then boiling with a large excess of sulphuric acid to expel the nitric acid, and making up to the strength of a decinormal solution of iron in about a quinquenormal sulphuric acid. The calcium and potassium sulphate solutions serve for tests and controls. In use, 10 c.c. of the decinormal solutions of barium nitrate, potassium chromate, and silver nitrate are added successively to 70 c.c. of the liquid under examination, contained in a tall 200 c.c. stoppered bottle, shaking vigorously for one minute after each addition. The mixture is preferably allowed to subside, or may be filtered, and 20 c.c. of the clear liquid is mixed with a measured excess of decinormal sodium chloride, and titrated back with centinormal silver nitrate, using potassium chromate as indicator. From the data obtained, the content of sulphuric acid is calculated. The liquid tested should have the strength of a centinormal solution; if stronger, it should be diluted, if weaker, concentrated, or the centinormal reagents employed throughout. Moreover, as a preliminary, substances precipitating barium or chromates, or reducing the latter, also ammonia, &c., must be eliminated, and any haloids present must be estimated, for which purpose the thiocyanate and ferric sulphate are provided. In estimating barium, the 70 c.c. of liquid under examination being of suitable strength, is first shaken with 10 c.c. of decinormal potassium sulphate, then the excess of sulphuric acid is estimated in the above manner.

D. A. L.

**[Estimation of Nitric and Ammoniacal Nitrogen in Plants.]** By AIMÉ PAGNOUL (*Ann. Agr.*, 1896, **22**, 485—490).—See this vol., ii, 120.

**Wet Method for Estimating Carbon and Nitrogen in Organic Compounds.** By PAUL FRITSCH (*Annalen*, 1896, **294**, 79—88).—The derivatives of isoquinoline described by the author (Abstr., 1895, i, 624) were analysed by a new method, which combines Messinger's process for estimating carbon (Abstr., 1889, 80; 1890, 1467) with Krüger's modification of Kjeldahl's method for determining nitrogen (Abstr., 1894, ii, 258).

The substance to be analysed is oxidised by means of potassium dichromate and concentrated sulphuric acid in a small distilling flask through which a current of purified air is passing. The gas produced is then passed into a heated combustion tube 36 cm. in length, containing a mixture of granulated copper oxide and lead chromate between two copper spirals. After being dried with calcium chloride, the carbonic anhydride is absorbed by potash. The residue in the flask is transferred to a larger distilling flask, connected with a Liebig's condenser, and the ammonia liberated on treatment with caustic soda is determined in the ordinary manner.

Figures illustrate the form of apparatus employed, and analytical details are described in the paper.

M. O. F.

**Analysis of Mortars.** By WILLIAM J. DIBDIN and ROBERT GRIMWOOD (*Analyst*, 1896, 21, 197—204).—The authors have analysed a large number of limestones, bricks, and mortars, and have tabulated the results.

In estimating lime and sandy matter in mortars, it must be remembered that, in practice, the mortars are made by volume and not by weight. The best plan, therefore, is to prepare a mortar according to the particular specification and to analyse this side by side with the inspected sample, allowing, of course, for difference in moisture, &c. The authors also give convenient factors for reducing the weights to volumes.

Earthy matter is estimated by treating the sample with dilute hydrochloric acid and repeatedly decanting from the heavy sandy matter; the earthy matter is then filtered, dried, and weighed. The filtrate contains the soluble silica, calcium, &c., which are then estimated as usual. From the amount of the former, a very fair idea as to the quantity of added cement may be obtained. L. DE K.

**Colorimetric Estimation of Lead.** By MAURICE LUCAS (*Bull. Soc. Chim.*, 1896, [3], 15, 39—42).—The author describes a method for estimating very small quantities of lead in alloys, &c. The lead and copper are separated by electrolysis, using a current of 0·3 ampère and 2 volts.; the lead, which is deposited on the positive pole in the form of peroxide, is, after washing, drying, and weighing, redissolved in 1 c.c. of the nitric acid containing nitrous acid, obtained by the electrolysis of nitric acid. The solution is rendered neutral with caustic soda and diluted so that 50 c.c. of water contains about 1 milligram of lead; five drops of ammonium sulphide is now added, and the colour of the liquid compared with that of solutions containing the same quantity of sodium nitrate and ammonium sulphide, to which different quantities of a standard solution of lead nitrate have been added.

Sodium carbonate and neutral salts have a considerable effect on the colour of the lead sulphide, consequently great care must be taken to keep the conditions exactly the same in the different solutions. M. W. T.

**Volumetric Estimation of Lead.** By FREDERICK J. POPE (*J. Amer. Chem. Soc.*, 1896, 18, 737—740).—The lead should be in the form of acetate. Lead sulphide (galena) is first converted into sulphate by the action of mixed nitric and sulphuric acids, and after removing the free acid, it is dissolved in ammonium acetate; the lead is now precipitated by adding an excess of standard solution of potassium dichromate, and the lead chromate is filtered off. The excess of chromate is then estimated by adding an excess of standard arsenious acid solution and a little dilute sulphuric acid, stirring until the yellow colour has completely disappeared or changed to a faint green; after adding a slight excess of sodium hydrogen carbonate, the excess of arsenious acid is titrated with standard solution of iodine. The calculation will be easily understood. The test analyses are remarkably accurate. L. DE K.

**Estimation of Iron and Aluminium Oxides in Phosphate Rock.** By THOMAS S. GLADDING (*J. Amer. Chem. Soc.*, 1896, 18,

717--721 ; 721—724).—Four grams of the finely-ground sample is heated for half-an-hour with 30 c.c. of dilute hydrochloric acid (1—1). This will leave any iron pyrites undissolved. After filtering, the iron is fully oxidised with nitric acid, and the liquid made up to a definite bulk.

An aliquot part of the solution, representing, say, one gram, is neutralised with ammonia and well cooled; more ammonia is then added until a permanent precipitate has formed, and this is again dissolved by cautiously adding hydrochloric acid. 15 c.c. of ammonium acetate (made by neutralising 30 per cent. acetic acid with ammonia) and 5 c.c. of acetic acid are placed in a beaker, and the phosphate solution is slowly added, with constant stirring. After keeping it at 60° for about an hour, the precipitate is collected and washed with a 10 per cent. ammonium acetate solution, redissolved in a few c.c. of hot hydrochloric acid (1—4), and one gram of ammonium phosphate is added. Ammonia is added until the liquid is turbid, then hydrochloric acid until the precipitate just redissolves, and the liquid is again poured into 15 c.c. of ammonium acetate and 5 c.c. of acetic acid. The precipitate formed is treated again in the same way, when a product is obtained free from calcium and consisting of normal aluminium phosphate with normal iron phosphate. The two are weighed together, and the iron phosphate is estimated volumetrically.

In another method, the solution is made as detailed above, but instead of using ammonium acetate, it is run into a solution of potassium hydroxide (500 grams per litre), and heated at 70° for about an hour. From the filtrate, the aluminium is recovered by first adding ammonium phosphate, then hydrochloric acid in slight excess, and precipitating the aluminium phosphate from this solution by means of acid ammonium acetate in the way already described. The iron may be estimated in the precipitate produced by the potash. L. DE K.

**Estimation of the Iron in Blood for Clinical Purposes.** By ADOLF JOLLES (*Montash.*, 1896, **17**, 677—696).—The first method described is as follows. A suitable quantity of the blood is evaporated to dryness, the residue strongly ignited, and then dissolved by fusing it with perfectly anhydrous potassium hydrogen sulphate, about 1 gram of the latter being used for each c.c. of blood originally taken; the operation is best conducted in a platinum crucible, but one of good Berlin porcelain may be used. The contents of the crucible are then rinsed with hot water into a beaker, poured into a flask, treated with dilute sulphuric acid and pure zinc (the amount of iron in which has been previously estimated; about 1 gram of zinc is used for every 1—2 c.c. of blood taken), boiled until all the zinc has dissolved (the flask being closed with a Bunsen valve), and the amount of iron finally titrated with N/50 or N/100 permanganate. In 10 samples of the blood of one and the same pig, the amount of iron found, per 1,000 grams of the blood, varied from 0·662 to 0·687; in the blood of eight different pigs, it varied between 0·549 and 0·948.

A second method is to evaporate the strongly ignited residue from 3—5 grams of the blood several times with strong hydrochloric acid

on the water bath, dissolve the residue in water, and precipitate in the cold with a solution of nitroso-$\beta$-naphthol (1—2 grams of the pure crystallised substance in 100 c.c. of 50 per cent. acetic acid), using about 5 c.c. of the solution per 3 grams of blood taken. The very bulky precipitate is collected, washed with small quantities of 50 per cent. acetic acid, dried at 100° and finally ignited, the residual ferric oxide being weighed. The whole operation requires about 45 minutes, and the results agree well with those obtained by the first method.

A third colorimetric method is recommended for clinical purposes. It requires two similar Nessler cylinders, graduated up to 15 c.c., and furnished with taps near the bottom; also a ferric solution, for purposes of comparison, made by fusing 0·0358 grams of pure ferric oxide with 50 grams of anhydrous potassium hydrogen sulphate, dissolving the product in water and making up to 500 c.c. 0·05 c.c. of blood is measured in a capillary pipette, rinsed out into a crucible, and evaporated to dryness; the residue is strongly ignited and fused with 0·1 gram of potassium hydrogen sulphate, and the cooled mass is rinsed with hot water into one of the cylinders and diluted to the 10 c.c. mark, whilst in the other cylinder 1 c.c. of the ferric solution is placed, and diluted to 10 c.c. To each cylinder is then added 1 c.c. of dilute hydrochloric acid (1 : 3), and 4 c.c. of ammonium thiocyanate solution (7·5 grams per litre), and the liquid is run out from the more deeply-coloured solution until the tint is seen to be the same on looking down through the two solutions. In this way, the amount of iron in the blood can be calculated, the specific gravity of the blood being also determined, if required, by Hammerschlag's method (*Zeitschr. klin. Med.*, **20**, 244), which requires only a single drop of blood. The percentage amount varied, in 10 adult men, between 0·526 and 0·720; in one anæmic man, it was only 0·441, and in an anæmic woman, 0·433. The results by this method agree well with those obtained by the other two methods, and 10—15 minutes suffice for making the experiment. C. F. B.

**Volumetric Estimation of Molybdenum and of Vanadium.** By Carl Friedheim (*Ber.*, 1896, **29**, 2981—2985).—Mainly a reply to Gooch and Fairbanks's criticisms (this vol., ii, 76), on the method previously described by the author and Euler (Abstr., 1895, ii, 535). The author shows that as good results can be obtained by his simpler method (*loc. cit.*) as by Gooch and Fairbanks's more complex one, provided the mixture is not heated too rapidly, so that no hydrogen iodide may be evolved before the air in the flask has become replaced by iodine vapour. The heating need only be continued until the liquid becomes clear green; further heating, as recommended by Gooch and Fairbanks, is useless. J. J. S.

**Solubility of Bismuth Sulphide in Sodium Sulphide; Estimation of Small Amounts of Bismuth in Anti-Friction Alloys.** By Thomas B. Stillman (*J. Amer. Chem. Soc.*, 1896, **18**, 683—684).—The author has found that bismuth sulphide is sensibly soluble in solution of sodium sulphide (sp. gr. 1·06) at the boiling temperature. If, when analysing an alloy containing but a few per cent. of bismuth, the neutralised solution is boiled as usual with

75 c.c. of the sodium sulphide, the loss in bismuth will be very great, whilst fractions of a per cent. may escape detection altogether.

L. DE K.

**Estimation of Ethylene in the Presence of Benzene Vapour.** By FRITZ HABER and H. OECHELHÄUSER (*Ber.*, 1896, **29**, 2700—2705). —Ethylene is completely absorbed by bromine water, as Treadwell and Stokes have stated, although this is denied by Winkler. Benzene, too, is almost entirely removed by this treatment, but in a purely mechanical manner; no chemical action takes place, for bromine vapour mixed with benzene vapour can be exposed to diffused light for 2 minutes without any loss of bromine occurring. It is thus possible to estimate the amount of ethylene by absorbing with a measured quantity of bromine water of known strength, and determining the residual bromine; this was done by treating the bromine water, while still in the burette, with potassium iodide, and subsequently titrating with thiosulphate. The bromine water was sucked into the (Bunte) burette through the lower tap, and its volume measured in the burette itself, the volume between the lowest graduation and the stop-cock having been previously determined. In this way, the Carlsruhe coal-gas was found to contain 3·85 per cent. of ethylene; the contraction, after treatment with bromine water and the addition of potassium iodide, was 4·4 per cent.; the difference is, of course, benzene.

C. F. B.

**Limiting the Explosive Proportions of Acetylene and Detecting and Measuring the Gas in the Air.** By FRANK CLOWES (*Chem. News*, 1896, **74**, 188).—The author's determinations show that the limits of explosiveness of mixtures of acetylene and air are reached with 3 and 82 per cent. of the former gas; from 22 per cent. upwards, the burning is accompanied by the separation of carbon. The corresponding limits for hydrogen are 5 and 72, for methane, 5 and 13. Even in quantities far below the explosive limit, acetylene tinges the author's standard hydrogen flame a yellowish green, and gives a well-defined, pale bluish "cap," which with a hydrogen flame 10 mm. high, attains a height of 17, 19, 28, and 48 mm. for 0·25, 0·5, 1, and 2 per cent. of acetylene respectively, whereas 2·5 and 2·75 per cent. of that gas give caps 56 and 79 mm., in height over a 5 mm. hydrogen flame. D. A. L.

# General and Physical Chemistry.

**Stereo-chemical Spectrometric Researches, I.** By JULIUS W. BRÜHL (*Zeit. physikal. Chem.*, 1896, 21, 385—413; *Ber.*, 1896, 29, 2902—2913).—The author has determined the molecular refraction and dispersion in the case of a number of stereoisomeric compounds. In the case of those compounds which could not be examined in the liquid state, solutions were prepared, and it was observed that, in order to obtain the best results, the solvent should have a refraction and dispersion as nearly as possible equal to those of the compound itself.* The compounds examined were: (I) monobromo-$\psi$-butylene, dimethylacetylene hydrobromide; $\alpha$-tolane dichloride, $\beta$-tolane dichloride; *syn*-anisaldoxime, *anti*-anisaldoxime; $\alpha$-benzilmonoxime, $\beta$-benzilmonoxime; $\alpha$-nitroformaldehyde-hydrazone, $\beta$-nitroformaldehyde-hydrazone; and (II) cinnamic acid, allocinnamic acid, cinnamylideneacetic acid, allocinnamylideneacetic acid; methylic cinnamate, methylic allocinnamate, ethylic cinnamate, ethylic allocinnamate; *anti*- and *syn*-metadibromodiazobenzene cyanide. The compounds may be divided into two classes, as indicated, in the first of which the refraction and dispersion are equal, or nearly so, the differences being usually within the experimental errors; these compounds include haloids, oximes, and hydrazones. In the second class, which includes acids, ethereal salts, and diazo-compounds, the values of the spectro-constants do not agree, and in this heterospectric class, it is noteworthy that, in every case, the higher melting, less soluble compound has the greater refraction and dispersion. In all cases, the observed numbers are considerably higher than the values calculated from the chemical composition; this is probably due to the elevating influence of the ethylene-phenyl unions. Similar results had been obtained by Walden (Abstr., 1896, ii, 633) in the case of the fumarates and maleates, but the author considers that further research is necessary before deciding whether the differences in the heterospectric compounds are due to a real difference of constitution.

L. M. J.

**Changes of Rotation in the Passage from Acid to Lactone.** By W. ALBERDA VAN EKENSTEIN, W. P. JORISSEN, and L. THEODORUS REICHER (*Zeit physikal. Chem.*, 1896, 21, 383—384).—The rotations of a number of acids and of the corresponding lactones were determined, and the numbers obtained are given in the accompanying table, the values for the molecular rotation being divided by $10^3$.

* This was observed by Perkin to obtain also in the case of the magnetic rotation. (Trans., 1896, 1056.)

| Acid. | Mol. rotation of | | Diff. |
|---|---|---|---|
| | Ion. | Lactone. | |
| Ribonic ............... | +0·2° | −3·0° | 3·2° |
| Gluconic (*d*) ......... | +1·3° to +1·8° | +11° to 12·1° | 10·8° to 9·2° |
| Mannonic (*d* and *l*)... | +2·0° | −9·5° to −9·8° | 11·7° |
| Saccharinic.......... | −1·1° | +15·2° | 16·3° |
| Isosaccharinic ...... | −1·1° | +10·2° | 11·3° |
| Saccharic ........... | +2·6° | +7·3° to 8·0° | 9·9° to 10·6° |
| Mannosaccharic...... | +0·2° | +35·1°−35·6° | 35·2° |
| α-Rhamnohexonic ... | +1·3° | +16·3° | 15·0° |
| α-Glucoheptonic...... | +1·6° | −11·2° | 12·8° |
| Gulonic (*d* and *l*) ... | ±2·7° | ∓9·9° | 12·6° |

L. M. J.

**Spectrum of Chlorophyll.** By ALEXANDRE L. ÉTARD (*Compt. rend.*, 1896, **123**, 824—828).—Knowledge of chlorophyll can only be extended by examination of large quantities of a chlorophyll of definite chemical composition. As a matter of fact, chlorophylls are comparatively stable compounds, and can be treated with ordinary reagents for the purpose of elucidating their chemical structure. In spectroscopic examinations, it is essential that the chlorophyll be a definite chemical species, dissolved in definite proportion in a given solvent, and examined in a layer of definite thickness.

The author gives drawings of the spectra of α-medicagophyll, $C_{28}H_{45}NO_4$, dissolved in carbon bisulphide and in alcohol of 90°, and of α-borragophyll, $C_{34}H_{53}NO_{12}$, in the same solvents, the concentrations in each case being 1 : 400, 1 : 1000, 1 : 10000.

Mere variations in the thickness or concentration of the solution examined are sufficient to cause one chlorophyll to be taken for another. In solutions of 1 : 10000, only the principal orange band remains visible. In carbon bisulphide, the bands are displaced towards the red as compared with the alcoholic solution, but they are particularly well-defined. The spectra of medicagophyll from lucerne and borragophyll from borage are distinctly different in the number and position of the bands; the former shows three bands between the general absorption at the red and violet ends, the latter five. C. H. B.

**Chemical Action of the Röntgen Rays.** By ALEXANDER VON HEMPTINNE (*Zeit. physikal. Chem.*, 1896, **21**, 493—496).—The electric conductivities of a number of salt solutions were determined, and no alteration was found to occur when the solutions were placed in the path of the Röntgen rays. In the case of solutions sensitive to light, such as silver nitrate in alcohol, and mercuric chloride with ammonium oxalate, the results obtained were doubtful, the effect, if any, of the rays being extremely small. The radiation was also found to have no effect on the velocity of hydrolysis of ethylic acetate, from which the author concludes that the Röntgen rays do not influence ionisation. A mixture of hydrogen and chlorine was not affected, and negative results were like-

wise obtained with a mixture of chlorine and carbonic oxide, so that their chemical activity appears to be very slight. L. M. J.

**Action of Metals and their Salts on Röntgen Rays.** By JOHN H. GLADSTONE and WALTER HIBBERT (*Chem. News*, 1896, **74**, 235).—The authors find that all metals transmit the Röntgen rays more or less, lithium being almost absolutely transparent, gold practically opaque, and there is every gradation between these two extremes; the order of absorption of the rays is that of the atomic weights, but the absorption increases more rapidly than the atomic weights. Metallic salts show absorption analogous to that of the metal; in fact, the absorption of a dry salt is the sum of the absorptions of its constituents. In solutions, the absorption seems to be that of the salt itself plus that of the solvent. D. A. L.

**Irreversible Cells.** By A. E. TAYLOR (*J. Physical Chem.*, 1896, 1, 1—20 and 81—90).—The author has continued the work of Bancroft (Abstr., 1894, ii, 4) on single-liquid polarisable cells, with especial reference to the effect of the negative ion on the potential difference between an electrode and the electrolyte in which it is immersed. The results confirm Bancroft's conclusion that, with mercury as one pole of the combination, the influence of the negative ion of the salt solution is appreciable, but concentration has no effect on the electromotive force of the cell. It has been shown by Gouy and others, on measuring single potential differences by means of the change of the surface tension of mercury, that an error might be introduced in some cases where there was the possibility of the formation of complex mercury salts. If dropping mercury electrodes do not always give correct results, the solution pressure of a metal is independent of the nature of the negative ion. In every case where the electromotive force of a cell appears to vary with the negative ion, the possibility of complex salts is present. The author concludes that the potential difference between a metal and an electrolyte is not a function of the negative ion of the salt solution, and that in certain cases dropping mercury electrodes do not give correct values for the single potential differences measured by that method. H. C.

**Hexamethylenetetramine Salts.** By MARCEL DELÉPINE (*Compt. rend.*, 1896, **123**, 888—891).—The author has determined the heats of saturation of hexamethylenetetramine by hydrochloric, sulphuric, nitric, and acetic acids, and the heats of dissolution of the hydrochloride, of the three sulphates, and of the two nitrates.

For the heats of saturation (1 mol. each of acid and base in 1 litre), the following numbers are given.

| | *Cal.* | | *Cal.* |
|---|---|---|---|
| $\frac{1}{2}HCl$ | 1·13 | $\frac{1}{2}HNO_3$ | 1·15 |
| $HCl$ | 2·13 | $HNO_3$ | 2·19 |
| $2HCl$ | 2·32 | $2HNO_3$ | 2·37 |
| $\frac{1}{4}H_2SO_4$ | 2·11 | $\frac{1}{2}C_2H_4O_2$ | 0·53 |
| $\frac{1}{2}H_2SO_4$ | 3·51 | $C_2H_4O_2$ | 0·81 |
| $H_2SO_4$ | 4·10 | $2C_2H_4O_2$ | 1·06 |

The addition of the second half equivalent of acid, therefore, produces less heat than the first. The results point to the slight dissocia-

tion of the neutral salt in solution. The following heats of dissolution of the base and its crystallised salts are given.

| | | | |
|---|---|---|---|
| $C_6H_{12}N_4$ cryst. | $+4{\cdot}80$ Cal. | $C_6H_{12}N_4,HNO_3$ | $-5{\cdot}5$ Cal. |
| $C_6H_{12}N_4,HCl$ | $-3{\cdot}94$ „ | $C_6H_{12}N_4,2HNO_3$ | $-14{\cdot}26$ „ |
| $C_6H_{12}N_4,H_2SO_4$ | $-1{\cdot}60$ „ | $C_6H_{12}N_4,H_2SO_4+H_2O$ | $-4{\cdot}71$ „ |

from which the following heats of formation are calculated,

| | | | | |
|---|---|---|---|---|
| $C_6H_{12}N_4$ | solid + | $HNO_3$ solid | $= C_6H_{12}N_4,HNO_3$ solid | $+19{\cdot}09$ Cal. |
| $C_6H_{12}N_4$ | „ | $+2HNO_3$ „ | $= C_6H_{12}N_4,2HNO_3$ „ | $+34{\cdot}63$ „ |
| $C_6H_{12}N_4$ | „ | $+\frac{1}{2}H_2SO_4$ „ | $= C_6H_{12}N_4,\frac{1}{2}H_2SO_4$ | $+16{\cdot}09$ „ |
| $C_6H_{12}N_4$ | „ | $+H_2SO_4$ „ | $= C_6H_{12}N_4,H_2SO_4$ | $+26{\cdot}11$ „ |
| $C_6H_{12}N_4,H_2SO_4$ | „ | $+H_2O$ liquid | $= C_6H_{12}N_4,H_2SO_4,H_2O$ | $+3{\cdot}11$ „ |
| $C_6H_{12}N_4$ | „ | $+HCl$ gas | $= C_6H_{12}N_4,HCl$ solid | $+28{\cdot}17$ „ |

The hydrochloride, nitrate, and sulphate are about equally stable in solution, the acetate apparently being more dissociated.

A. C. C.

**Heat of Formation of Selenic Acid and Selenates.** By René Metzner (*Compt. rend.*, 1896, **123**, 998—1000).—The heat of neutralisation of selenic acid by sodium hydroxide was found to be $+31{\cdot}19$ Cal., whilst the action of selenic acid on the normal selenate absorbs $-0{\cdot}70$ Cal. Thomsen found $+30{\cdot}39$ Cal. and $-0{\cdot}86$ Cal. respectively, and the corresponding numbers obtained by the author with potassium hydroxide were $+31{\cdot}31$ Cal. and $-1{\cdot}24$ Cal. The heat of neutralisation of the acid by barium oxide is $+36{\cdot}92$ Cal., by lead oxide, $+19{\cdot}81$ Cal.; and by silver oxide, $+18{\cdot}35$ Cal., these values being obtained by double decomposition.

The hydrate, $SeO_3,2H_2O$, was obtained by concentrating the acid under atmospheric pressure at a temperature below 210°, and purifying the first crystals by melting and recrystallisation; the monhydrate, $H_2SeO_4$, was prepared in a similar way, but the evaporation was in a vacuum. The calorimetric measurements gave the following results.

| | | | |
|---|---|---|---|
| $H_2SeO_4$ | sol. + Aq = $SeO_3$ diss. | develops | $+13{\cdot}35$ Cal. |
| $H_2SeO_4$ | liq. + Aq = $SeO_3$ „ | „ | $+16{\cdot}80$ „ |
| $SeO_3,2H_2O$ | sol. + Aq = $SeO_3$ „ | „ | $+7{\cdot}45$ „ |
| $SeO_3,2H_2O$ | liq. + Aq = $SeO_3$ „ | „ | $+12{\cdot}02$ „ |

hence the heat of fusion of $H_2SeO_4$ is $-3{\cdot}45$ Cal., and of $SeO_2,2H_2O$, $-4{\cdot}75$ Cal. and $H_2SeO_4$ sol. and $H_2O$ sol. = $SeO_3,2H_2O$ sol. develops $+4{\cdot}55$ Cal.

Combining these results with Thomsen's determinations, it follows that

$$\begin{cases} SeO_2 \text{ sol.} + O + H_2O = H_2SeO_4 \text{ diss. develops } + 19{\cdot}86 \text{ Cal.} \\ SeO_2 \text{ „ } + O + H_2O = H_2SeO_4 \text{ liq. „ } + 3{\cdot}06 \text{ „} \end{cases}$$

$$\begin{cases} Se + O_3 + H_2O = H_2SeO_4 \text{ diss. „ } + 76{\cdot}66 \text{ „} \\ Se + O_3 + H_2O = H_2SeO_4 \text{ liq. „ } + 59{\cdot}86 \text{ „} \end{cases}$$

$$\begin{cases} Se + O_4 + H_2 = H_2SeO_4 \text{ diss. „ } + 145{\cdot}66 \text{ „} \\ Se + O_4 + H_2 = H_2SeO_4 \text{ liq. „ } + 128{\cdot}86 \text{ „} \end{cases}$$

All the values, except those for hydration, are lower than the corresponding values for sulphuric acid.

C. H. B.

**Cryoscopic Researches.** By Karl Auwers and K. Orton (*Zeit. physikal. Chem.*, 1896, **21**, 337—377).—In order to further attest the

validity of the rules deduced by Auwers (Abstr., 1896, ii, 293), the authors have determined the cryoscopic behaviour of a large number of substituted phenols and also of oxyazo-compounds. The first set of experiments was on the effect of ortho-substituents on various para-phenolic compounds. The aldehyde-group has the most powerful "abnormalising" influence; the cyanogen and methylic carboxy-groups are nearly alike in their effects. Nitro-groups have the strongest "normalising" effect, whilst of the halogens, iodine has the most marked influence. The cryoscopic behaviour of the orthohydroxyazo-compounds leads the authors to the conclusion that these compounds are not phenols, but hydrazones of orthoquinone. The researches were then extended to the derivatives of benzoic acid, but here the influence of the substituent is less marked, as almost all the compounds examined are abnormal, the variations from normal value increasing with the concentration. L. M. J.

**Abnormal Freezing Point Depressions.** By GUIDO BODLÄNDER (*Zeit. physikal. Chem.*, 1896, **21**, 378—382).—In the experiments made by Ciamician and Garelli on the formation of solid solutions in the case of anthracene and salicylic acid in benzoic acid, the concentration of the salicylic acid in the solid solution was compared with that in the *original* solution, whereas the author points out that comparison should have been made with the solution with which the crystals were in equilibrium; on making this correction, he finds that the ratio is not constant, but varies from 0·68 to 1·08. Similarly, in the experiments with benzene, phenol, and benzil, the ratio of the concentration of the phenol in the solid and liquid solutions varies from 0·309 to 0·198, increasing with dilution. If the molecular weight in the solid phase is calculated from these numbers, it is found to be smaller than that in the liquid, and on the assumption that the solid contains simple molecules, and the liquid simple and double molecules, the author calculates the dissociation of the latter; the results appear to be in accordance with the laws of mass action, but the author does not consider that this must necessarily be the true explanation of them.
L. M. J.

**Compressibility of certain Gases at 0° and under nearly Atmospheric Pressure.** By ANATOLE LEDUC (*Compt. rend.*, 1896, **123**, 743—745).—The author has determined the compressibility of five gases at pressures ranging from 35 cm. to 113 cm. of mercury, adopting Mariotte's method. The apparatus consisted of a manometer similar to that used by Regnault in the determination of the expansion of gases at constant pressure, with the addition, however, of a third tube, by means of which mercury could be admitted at will without introducing air bubbles. The gas was cooled by immersing the apparatus in a bath of ice-cold water, the temperature of which was accurately observed. Owing to the slight variations of pressure, the author substitutes $A(P - P_0)$ for $\epsilon$ in Regnault's expression,

$$\epsilon = \frac{P_0V_0}{PV} - 1,$$

representing the departure of a gas from Mariotte's law. Expressing

the pressure in centimetres, and taking $P_0 = 76$, the following values of the coefficient A are given.

*Carbonic anhydride.* $A = 102 \cdot 10^{-6}$, a number which is higher than that obtained by Regnault.

*Nitrous oxide.* $A = 11 \cdot 10^{-5}$ (approx.).

*Hydrogen chloride.* At 0°, $A = 120 \cdot 10^{-6}$ (between 76 cm. and 120 cm.).

At 15°, $A = 107 \cdot 10^{-6}$ (between 76 cm. and 120 cm.).

*Ammonia.* At 0°, $A = 243 \cdot 10^{-6}$ (between 76 cm. and 130 cm.).

At 14°, $A = 190 \cdot 10^{-6}$.

*Sulphurous anhydride.* $A = 323 \cdot 10^{-6}$.

The following coefficients of expansion of gaseous ammonia between 0° and 14° are given.

| | |
|---|---|
| Const. press. of 115 cm. | 0·00404 |
| Const. press. of 76 cm. | 0·00389 |

A. C. C.

**Potential Energy and Virial of Molecular Forces.** By G. Bakker (*Zeit. physikal. Chem.*, 1896, 21, 497—506).—By consideration of the potential energy in a liquid, the author deduces that the ratio between the heat of vaporisation and the difference between the liquid and gaseous densities is proportional to the square of the diameter of the molecules, and hence, under certain conditions, the latter may be compared. L. M. J.

**New Method of Determining the Specific Gravity of Liquids.** By Roman Zaloziecki (*Zeit. angw. Chem.*, 1896, 552—556). —The principle of the method has already been taken advantage of by Boyle and by Babinet to compare the specific gravities of two different liquids. The author's apparatus consists essentially of a long U-tube, one of the arms of which is calibrated, whilst a stop-cock, a little above the bend, separates it from the bend and the other arm. If the sp. gr. of an aqueous solution is required, the uncalibrated limb is filled with a liquid of low sp. gr., and immiscible with water, such as light petroleum, which answers very well. The aqueous liquid is run into the calibrated tube to a fixed height, and, by opening the tap, the two liquids are brought into contact. The apparatus is plunged for some time in water at 15°, and the difference in the height of the two columns is then recorded in mm. For instance, if the column of aqueous liquid measures 502 mm. (= 500 mm. + 2 mm. allowance for effect of capillarity in a tube 5 mm. broad), its sp. gr. is found by multiplying the difference by 2, adding 1000, and multiplying this by the sp. gr. of the light petroleum. The apparatus may, of course, be used for petroleum, oils, &c.; in this case, water is used in the uncalibrated limb instead of light petroleum. L. de K.

**Solution and Fusion.** By Wilder D. Bancroft (*J. Physical Chem.*, 1896, 1, 137—148).—The author discusses the question whether solubility and fusion curves are always identical, or ever so. It is evident that solubility curves cannot in all cases be fusion curves, as the temperature of the experiment is above the fusion temperature of either of the components in many cases. Even where this is not the case, the

author holds that there is a distinction between a fusion curve and a solubility curve. The approximation formulæ for the change of concentration with the temperature have the same form for both curves except that the heat of fusion enters into one, and the heat of dissolution into the other. Since these two quantities are not identical, it follows that there is a radical distinction between the two curves. The partial pressure of the solvent is always less than its vapour pressure as a pure liquid at the same temperature; it is therefore possible for the vapour pressure of the dissolved substance (solute) to be greater or less than its vapour pressure in the pure state, depending on conditions with which we are not yet familiar. Even when two liquids are miscible in all proportions (consolute), it appears that each may still have a definite solubility one in the other. H. C.

**Some Abnormal Cases of Solubility.** By HENRI L. LE CHATELIER (*Compt. rend.*, 1896, **123**, 746—749).—When certain metallic sulphates are added in increasing quantities to sodium sulphate, the curve representing the melting points of the various mixtures is different in character from those plotted by the author for the mixtures of salts previously examined (comp. Abstr., 1894, ii, 272, 307). In the case of the sulphates of calcium and magnesium, the following numerical results are given, 875° being the melting point of sodium sulphate.

$Na_2SO_4 + CaSO_4$—

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Concentration ... | 0 | 1 | 3 | 5 | 7·5 | 10 | 20 | 30 | 40 |
| Temperature ..... | 875° | 884° | 900° | 912° | 923° | 930° | 941° | 938° | 923° |
| | 46 | 51 | 54 | 57 | 67 | 75 | 100 | | |
| | 912° | 905° | 925° | 950° | 1040° | 1130° | (1350°). | | |

$Na_2SO_4 + MgSO_4$—

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Concentration ... | 0 | 5 | 15 | 30 | 35 | 42 | 48 | 50 | 55 |
| Temperature ..... | 875° | 870° | 830° | 740° | 690° | 655° | 675° | 700° | 730° |
| | 67 | 70 | 75 | 80 | 100. | | | | |
| | 800° | 795° | 870° | 925° | 1170°. | | | | |

The effect of the addition, therefore, of the first small proportion of these two sulphates is either to raise the melting point of the mixture, or at least to produce no appreciable lowering. It is probable that this abnormal behaviour is due to the isomorphism of sodium sulphate with the double sulphates formed. When certain fused mixtures of the above sulphates are allowed to solidify, the mass remains transparent even to the point of complete solidification, owing to the formation of crystals which are all of the same nature. The curves representing the melting points of mixtures of sodium sulphate with increasing proportions of the sulphates of calcium, barium, lead, magnesium, and cadmium consist of three parts, the first corresponding with the formation of isomorphous crystals containing the two constituents in varying proportions, the second to the formation of definite double sulphates, and the third to the crystallisation of the added sulphate itself.

A. C. C.

**Precipitation of Salts.** By H. A. BATHRICK (*J. Physical Chem.*, 1896, 1, 157—169).—Bancroft has shown that the solubility of salts in alcohol can be represented by an equation of the form $(x + A)\, y^n = C$, where $x$ and $y$ denote respectively the quantities of alcohol and of salt

in a constant quantity of water. The author finds by direct experiment that this equation holds for the solubilities of salts in aqueous alcohol and in acetone. The factor $n$ is apparently independent of the temperature. The term $A$ is a function of the salt, the solvent, and the temperature. If $x$ is expressed in reacting weights, the product of $A$ into the reacting weight is independent of the nature of the substance denoted by $x$. H. C.

**The Neutrality of Salts and Coloured Indicators.** By HENRI LESCŒUR (*Compt. rend.*, 1896, 123, 811—813).—The author discusses the precise significance of the colour changes of certain indicators. He points out that the formation of a blue colour with litmus indicates the presence of excess of alkali, and not neutrality. When an alkali is added to a solution of a salt of an insoluble oxide in presence of litmus, the change to blue takes place, not when all the free acid has been neutralised, but after all the oxide has been precipitated and the alkali is in excess. In many cases, the colour of the litmus changes continuously from red to blue. The behaviour of litmus with alum and other salts clearly shows that the red colour indicates neutrality as well as acidity.

In the case of phenolphthalein, the production of the red colour indicates, not the passage from acidity to alkalinity, but from neutrality to alkalinity.

Helianthin (Poirrier's orange No. 3) is colourless in neutral or alkaline solutions, and red in presence of acids. This indicator, therefore, shows the passage from neutrality to acidity.

The author considers that a really neutral substance is one with which phenolphthalein and helianthin both remain colourless, whilst litmus remains red. C. H. B.

**Speed of Etherification, as compared with Theory.** By ROBERT B. WARDER (*J. Physical Chem.*, 1896, 1, 149—156).—The theory of mass action is applied to Lichty's experiments (Abstr., 1896, ii, 557) on the speed of etherification, in which equivalent weights of ethylic alcohol and the several chloracetic acids were made to react for definite intervals at 80°. Numbers are given proportional to the coefficient of speed, as obtained by integration between the limits of successive determinations. They show the same general features for each acid; a steady decrease in the early stages is followed by a moderate increase, then by a rapid fall. Further experiments are needed to determine the cause of the secondary influences indicated before the actual constants can be determined and in order to trace the effect of successive atoms of chlorine in acetic acid. H. C.

**Catalytic Hydrolysis by Metals.** By BOHUSLAV RAÝMAN and OTTOKAR ŠULC (*Zeit. physikal. Chem.*, 1896, 21, 481—492).—The effect of temperature on the inversion of sugar by pure water was first studied, a platinum flask provided with a reflux platinum condenser being employed. At 60°, no change occurred in 50 hours; at 80°, the rotation fell from $+11{\cdot}56°$ to $+0{\cdot}31°$ in 58 hours, and at 100° reached $-3{\cdot}42°$ in 25 hours. Rotation/time curves are constructed in each case, from which it is seen that the velocity of inversion is at first

small, then increases, and again diminishes towards the close of the reaction. In glass vessels, the velocity is considerably less, and the effect of metals other than platinum was, therefore, investigated by the use of similar copper and silver flasks, when the rate of inversion was found to be slightly less than in the platinum vessel and less in the copper than in the silver flask. The solution in the copper flask became slightly acid and turbid owing to traces of finely-divided copper. The effect of finely-divided metals of the platinum group was investigated, hard glass flasks being used, and curves are given as before. An increase of velocity was obtained in each case, except that of iridium, the accelerative effect of palladium being extraordinarily great. The effect is probably due partly to a specific action of the metal and partly to acids formed by oxidation. The decomposition of glucose and fructose by water was therefore investigated, but found to be of a very complicated nature. L. M. J.

**Absorption. Water in Colloids, especially in the Hydrogel of Silicic Acid.** By JACOBUS M. VAN BEMMELEN (*Zeit. anorg. Chem.*, 1896, 13, 233—356).—In continuation of his researches on the composition and properties of inorganic oxides in the colloidal state (Abstr., 1894, ii, 191), the author has examined the conditions under which the absorption and elimination of water by the hydrogel of silicic acid take place at constant temperature. The process is a gradual and a continuous one, the elimination of water taking place, however, with greater difficulty the more nearly the substance approaches the anhydrous condition. The hydrogel appears to form an intermediate stage in the passage from the liquid to the solid condition during the separation of a dissolved colloidal substance from a solvent. This separation commences with the formation of the hydrosol, the solution usually remaining clear, but the dissolved substance exercising little or no influence on the osmotic pressure, boiling point, freezing point, or electrical conductivity. Solutions of colloids in this condition contain molecular groups which do not follow the laws which hold for crystalloids in solution, and determinations of the molecular weights of colloids in solution by the customary methods are therefore valueless. The formation of the hydrogel is indicated by the coagulation that occurs. It may be assumed that the semi-liquid particles of the colloid arrange themselves with the water molecules to form a cell-like structure of definite form, and that these cells hang together at certain points, so forming a network. The water is then retained, partly by the cells themselves, and partly in the interstices between the cells. The author shows that the general behaviour of the hydrogel of silicic acid is in keeping with these views. H. C.

**Theory of Corresponding States.** By G. BAKKER (*Zeit. physikal. Chem.*, 1896, 21, 507—508).—The paper contains a more rigid proof of the conclusions obtained in the author's previous paper (this vol., ii, 17) which involved certain tacit assumptions. L. M. J.

**Unit of Atomic Weights.** By KARL SEUBERT (*Zeit. anorg. Chem.*, 1896, 13, 229—232).—The author regards the result of Morley's

determination of the ratio O : H = 15·879 : 1 as probably correct to within 0·06 per cent. It may, therefore, now be regarded as proven that the atomic weight of oxygen (H = 1) is, for practical purposes, about 15·88. The use of this number, and the retention of the atomic weight of hydrogen as the unit, is advocated in place of the practice of fixing the atomic weight of oxygen as 16. H. C.

**The Discovery of New Elements during the last Quarter of a Century, and Questions relating thereto.** By CLEMENS WINKLER (*Ber.*, 1897, **30**, 6—21).—This paper is the report of a lecture delivered before the German Chemical Society, and traces the history of those elements which have been discovered during the last quarter of a century. M. O. F.

**A New Stirrer.** By HERMANN SCHULTZE (*Ber.*, 1896, **29**, 2883).—This consists of a glass rod, to one end of which two glass balls are hung by pieces of platinum-iridium wire. When the rod is rotated by a turbine, the balls fly asunder, stirring the liquid in which they are immersed. C. F. B.

## Inorganic Chemistry.

**Nascent Hydrogen.** By R. FRANCHOT (*J. Physical Chem.*, 1896, 1, 75—80).—Ferric sulphate was reduced in an electrolytic cell, using platinum as the cathode, and pure zinc, cadmium, or copper as the anode. As, on analysis, it was found that the reduction at the anode was equal to or even greater than that at the cathode, it became evident that zinc, cadmium, and copper reduce ferric sulphate directly. This was further confirmed by adding zinc, cadmium, and copper, to different portions of a carefully neutralised solution of ferric sulphate, when in all three cases considerable quantities of ferrous iron were formed. It appears, therefore, that, in the reduction of ferric salts in acid solutions by metals, there is a direct reduction by the metal and an indirect reduction due to the action of the acid on the metal. H. C.

**Action of Sulphuric Acid on Iodine and Iodic Acid.** By PAUL CHRÉTIEN (*Compt. rend.*, 1896, **123**, 814—816).—When iodic acid is dissolved in sulphuric acid at 200°, there is slight decomposition, and the crystals that separate on cooling are yellowish, but if some fuming nitric acid is added to the hot liquid, the crystals are white. They retain small quantities of sulphuric acid when dried on porcelain, but, if powdered and again dried, they contain 99·6 per cent. of iodic anhydride; this has not previously been obtained in a crystalline form.

When the solution of iodic acid in sulphuric acid is heated at 250—260°, oxygen and iodine are liberated, and a yellow, amorphous precipitate is formed which is instantly decomposed by water into iodine, iodic acid, and sulphuric acid. With prolonged heating, the liquid becomes black, and then, with extreme slowness, it deposits yellow crystals, which can also be obtained by dissolving iodine in a

hot solution of iodic acid in sulphuric acid. These crystals are decomposed by water in the same way as the amorphous products. The ratio of iodine to oxygen is 5·291, and of free iodine to iodine present as iodic acid 1·506. The crystals seem to have the composition

$$2SO_3,H_2O,2I_2O_3;$$

they are decomposed by water in accordance with the equations

$$3I_2O_3 + H_2O = 2I_2O_5 + 2HI \text{ and } I_2O_5 + 10HI = 6I_2 + 5H_2O,$$

the final result being $5I_2O_3 = 3I_2O_5 + 2I_2$.

Ogier found that the action of ozone on iodine converts it into a yellow powder, which is decomposed by water in the same way as the compounds described by the author. C. H. B.

**Ozone and Phosphorescence.** By MARIUS OTTO (*Compt. rend.*, 1896, **123**, 1005—1007).—Whilst ozonised air was being aspirated with a water pump, it was observed that the water became luminous, and retained its luminosity for five or six seconds. Flasks filled with the issuing water were, in fact, distinctly luminous.

It was found that, when water is shaken with ozonised oxygen, the phenomenon of luminescence can be reproduced five or six times and then ceases, but is observed again with the same quantity of gas if a fresh quantity of water is introduced. Increase or reduction of pressure has no appreciable effect on the luminosity. With alcohol of 90°, the luminescence is feebler but more persistent; with benzene, it is very feeble, and the ozone is completely absorbed or decomposed.

Thiophen yields abundant luminous vapours, and is the only compound that showed this peculiar phenomenon. With milk, the phosphorescence is much more intense than with ordinary water, and with urine, it was more intense than with any other compound examined. On the other hand, water carefully freed from organic matter showed no phosphorescence, even with highly concentrated ozone, and it follows that the phosphorescence observed with ordinary water is due to the action of the ozone on the vegetable or animal matter present in it. C. H. B.

**Action of some Hydrogen Compounds on Thionyl Chloride.** By J. ADOLPHE BESSON (*Compt. rend.*, 1896, **123**, 884—886).—Aluminium bromide reacts vigorously with thionyl chloride, the solution, when cooled, depositing crystalline double compounds of aluminium chloride and bromide with thionyl chloride; on distilling this under reduced pressure, thionyl bromide, solidifying at $-52°$, is obtained, but the yield is much smaller than is obtained by the method previously described by the author (Abstr., 1896, ii, 358). Hydrogen iodide reacts vigorously with thionyl chloride, according to the equation $2SOCl_2 + 4HI = 4HCl + 2I_2 + SO_2 + S$, even when cooled by a freezing mixture.

Hydrogen sulphide reacts slowly with thionyl chloride, according to the equation $2SOCl_2 + 2H_2S = 4HCl + SO_2 + 3S$, when cooled in a mixture of ice and salt, whilst at higher temperatures the main action is represented by the equation $2SOCl_2 + H_2S = S_2Cl_2 + SO_2 + 2HCl$. Gaseous hydrogen phosphide at ordinary temperatures causes an evolution of hydrogen chloride, the liquid, after some time, forming two

layers, the upper of which, on distillation under reduced pressure, yields, first, thionyl chloride, then phosphoryl chloride, and, finally, thiophosphoryl chloride, $PSCl_3$; a syrupy liquid from which no definite compound can be obtained remains in the retort. The lower layer is viscous, and contains chlorine, sulphur, phosphorus, oxygen, and hydrogen. It yielded no definite results on analysis.

A. C. C.

**Densities of Nitrogen, Oxygen, and Argon, and the Composition of Atmospheric Air.** By ANATOLE LEDUC (*Compt. rend.*, 1896, **123**, 805—807).—The author's determination of the density of nitrogen prepared by chemical methods gives 0·9671 as compared with air. Oxygen obtained by electrolysis of a solution of potassium hydroxide gives the number 1·10523, which is slightly lower than that previously given. The density of argon calculated from the density of air, and the constant proportion (0·0119) of argon in it, is 1·376, or 19·8 with reference to hydrogen.

The weight of a litre of oxygen at 0° and normal atmospheric pressure is 1·4293 grams; of nitrogen, 1·2507 grams; and of argon, 1·780 grams.

The composition of air by weight is, nitrogen, 75·5; oxygen, 23·2; argon, 1·3; and, by volume, nitrogen, 78·06; oxygen, 21·0; and argon, 0·94.

C. H. B.

**Presence of Nitrites in the Air.** By GEORGE DEFREN (*Chem. News*, 1896, **74**, 240—241).—Continuing these investigations (compare this vol., ii, 94), air tightly corked up for 12 to 24 hours in large bottles of over 8 litres capacity along with 100 c.c. of water, and occasionally shaken, yielded up all its nitrites to the water. Determinations made in this way showed that the presence of human beings in a room increases the proportion of nitrites in the air, and confirmed the similar effect of burning gas already noticed. Air from the lungs blown through water gave no evidence of nitrites; this, however, is not considered conclusive evidence of the absence of nitrites in expired air, inasmuch as air that yields nitrites when exposed over water, does not yield them when bubbled through water, this being attributed to the oxidation of the nitrites to nitrates by the large preponderance of oxygen in the gaseous mixture. Like previous investigators, the author finds the proportion of nitrites and nitrates in the air increased by thunderstorms, and reduced, by washing out, by rainstorms.

D. A. L.

**Transformations of Pyrophosphoric Acid.** By MARCELLIN BERTHELOT and GUSTAVE ANDRÉ (*Compt. rend.*, 1896, **123**, 776—782).—A solution of pyrophosphoric acid containing 15·6 grams of phosphoric anhydride per litre was prepared by the action of hydrogen sulphide on lead pyrophosphate, and was allowed to remain at the ordinary temperature, the proportion of pyrophosphoric acid being determined from time to time (this vol., ii, 158). Titrations with tropeolin and phenolphthalein showed that the solution contained no metaphosphoric acid, and that none of the latter was formed during the course of the experiments. One series of the experiments gave the following results.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Days ........................ | 2 | 5 | 10 | 19 | 52 | 89 | 110 | 121 |
| Percentage of pyrophosphoric acid remaining | 91 | 87 | 83 | 76·5 | 69·5 | 58 | 49·5 | 43·1. |

The conversion of pyrophosphoric into orthophosphoric acid proceeds continuously, but is very much slower than the hydration of metaphosphoric acid. Experiments with a solution of half the concentration gave similar results, and showed that the rate of change increases with the concentration. Similar results were obtained with pyrophosphoric acid prepared by the action of hydrochloric acid on silver pyrophosphate.

In order to ascertain whether pyrophosphoric acid can be obtained by the direct dehydration of the ortho-acid, some of the latter was heated and weighed from time to time, and when the ratio of phosphoric anhydride to water was 1 : 1·55, the product contained 56·4 per cent. of the phosphorus as pyrophosphoric acid, 29·8 per cent. as the ortho-acid, and 13·8 as the meta-acid. It follows that some metaphosphoric acid is formed even before all the ortho-acid has been converted into the pyro-acid, and, during the heating, a condition of equilibrium is established between the three acids. When the heating is carried further, the phenomena become very complex, owing to the polymerisation of the meta-acid. During the heating, there is a notable volatilisation of the solid matter, which, however, only becomes distinct when the meta-acid begins to form. C. H. B.

**Effect of the Presence of Boric Acid in Glass and Enamels.** By L. Grenet (*Compt. rend.*, 1896, **123**, 891—893).—When boric acid is added to glass and enamels, it increases their toughness and fusibility, and modifies their coefficient of expansion, sometimes increasing and at other times diminishing it. When increasing quantities of boric acid are added to glass, the coefficient of expansion at first diminishes and then increases, finally approaching that of boric acid itself.

Tables are given showing the coefficients of expansion of mixtures of the oxides of sodium, lithium, zinc, and lead, as also of white glass and bottle glass, with increasing quantities of boric acid. The amount of boric acid that can be added to glass without causing devitrification, on the one hand, or the separation of the added boric acid, on the other, depends on the nature of the metallic oxides and the proportion of silica contained in the glass, as well as on the rapidity with which the latter is cooled. A. C. C.

**Combustion of Illuminating Gas on Cooled Surfaces.** By Fritz Haber and A. Weber (*Ber.*, 1896, **29**, 3000—3006).—According to Lewes (Abstr., 1892, 407), appreciable quantities of unburnt gas arise from the combustion of illuminating gas on cooled surfaces; the authors, however, consider that this result is due to an insufficiency of oxygen, and have, therefore, repeated the investigation. They state the results of numerous experiments carried out with a Teclu gas-burner and with various forms of gas-stove, and appear to arrive at the same conclusion as Lewes. An explanation of the presence of unburnt gas is put forward in the paper. M. O. F.

**The Development of the Soda Manufacture and Allied Industries in the last 25 Years.** By ROBERT W. HASENCLEVER (*Ber.*, 1896, **29**, 2861—2877).—This period stretches roughly from the development of the ammonia-soda process to the realisation of an electrolytical method for the preparation of soda. The paper under review contains very brief notices of the more important innovations during this period, and gives references to sources where details of the methods introduced may be found.

*Sulphuric Acid manufacture.*—Pyrites is still the chief source of the sulphur. The German ore, the consumption of which has remained fairly constant, contains zinc, and this is recovered from the roasted ore by an electrolytical method. Spanish ore is more and more imported into Germany; 1 ton of it yields 610 kilos. of iron oxides, 34 kilos. of copper, $29\frac{1}{2}$ grams of silver, and $\frac{1}{10}$ gram of gold. Some works are erecting blast-furnaces for smelting the iron oxides, which they find a difficulty in selling. A successful method of utilising zinc blende for the manufacture of sulphuric acid has also been worked out. In the construction of the leaden chambers, of the acid pumps, and of other apparatus, great advances have been made, the chemist having called in the engineer to his aid. Lunge, guided by some of his researches, has even proposed to substitute earthenware towers with perforated plates for the leaden chambers. The chamber acid is still concentrated at first in leaden pans, the final concentration being carried out, as a rule, in platinum vessels on the Continent, whilst in England glass vessels are still largely used. Lunge has patented a method by means of which a concentrated acid is made, by cooling it to about $-20°$, to yield crystals of $H_2SO_4$, a weaker acid beng left behind. Sulphuric anhydride is now made on the large scale, and cheaply; the best way is to obtain a solution of sulphurous anhydride by passing through water the gases given off from the furnaces in which pyrites is roasted, to heat this solution, and pass a mixture of the evolved gas with air under increased pressure over platinised asbestos.

*Hydrochloric Acid and Chlorine.*—On the Continent, where the ammonia-soda process has almost entirely replaced the old Leblanc process, the price of hydrochloric acid has risen greatly, and certain branches of industry that depended on it have had to be given up. In England, however, no great rise in price has taken place, so that, in this country, chlorine is still largely made by the Weldon process, although the Deacon process has of late begun to find a wider development; the latter process is now the one chiefly used on the Continent. One of its defects is, that the conversion of the hydrogen chloride is not complete, and a weak solution of this gas is obtained as a bye-product; the use of sulphuric acid has been introduced to regenerate the gas from this solution.

The ammonia-soda manufacturers have made many attempts to obtain chlorine from the bye-products formed in that process. The only method which has been attended with any measure of success is that of Mond, who freezes out the ammonium chloride from the solution of it obtained in working the ammonia-soda process, volatilises it in vertical cast-iron retorts lined with thin tiles, passes the vapour into vertical wrought-iron cylinders packed with balls of magnesia (containing a little kaolin and calcium chloride) heated to a temperature of 300°, and drives out the

ammonia by means of the gases resulting from the calcination of sodium hydrogen carbonate; these gases contain no oxygen, and being heated by passing first through a regenerator, they raise the temperature of the magnesia decomposer to 600°. Air is then passed into the decomposers at this temperature, and a gas containing 18—20 per cent. by volume of chlorine is obtained; finally, the decomposers are cooled to 350° by a current of cold air, and ammonium chloride vapour is then again introduced. As regards the chemical reactions involved, the ammonium chloride vapour reacts with the magnesia, yielding magnesium chloride, together with ammonia and water, which pass on. The magnesium chloride is then decomposed by the oxygen of the air, chlorine being formed and magnesia regenerated. Mond is, however, not extending this process as rapidly as he would otherwise have done, on account of the introduction of electrolytical methods for the preparation of chlorine. In the manufacture of bleaching powder, mechanical methods have been largely introduced; lime, fed in at one end of a system of pipes, is made to travel through these by an endless screw, meeting a current of chlorine as it does so, and is delivered as bleaching powder at the other end of the system.

*Soda.*—In Germany, France, Austria, and England, 13, 16, 36, and 50 per cent. respectively of the total output is still manufactured by the old Leblanc method; in this method, the chief advance consists in the introduction of mechanical furnaces, in place of working the charges by hand. Hargreaves has developed a method by which sodium sulphate is made directly, without the intervention of sulphuric acid, by the action of sulphurous anhydride, steam, and air on salt in iron cylinders; the products are sodium sulphate and hydrochloric acid. This process is worked to some extent in England, and also at one or two works in France and Germany. The recovery of the sulphur from the waste of the Leblanc process was at one time effected by letting the waste stand with water in tanks through which air was blown, and then decomposing the resulting extract with hydrochloric acid, when sulphur was precipitated. This process, due to Schaffner and Mond, is now less used, on account of the rise in price of hydrochloric acid. Chance has worked out a process in which the soda waste is treated in cylinders with the gases obtained by burning limestone; hydrogen sulphide is formed, and this is burned to sulphur and water in a Claus furnace, whilst the calcium carbonate remaining in the cylinders is used for making cement. This method is worked in England, but not very widely. In the ammonia-soda process, the chief advances have been in the increase of the output of an installation, and in diminishing the loss of ammonia.

C. F. B.

**Lithium Nitride.** By Antoine Guntz (*Compt. rend.*, 1896, **123**, 995—997).—Lithium combines with nitrogen with incandescence when heated in a stream of the gas, but the product is impure, because the dish holding the lithium is attacked. Iron, nickel, silver, platinum, rock crystal, and graphite are all acted on somewhat readily. A much purer product is obtained by heating the lithium very gently in an iron dish in a very slow current of nitrogen, but in this case some of the lithium may remain uncombined. It is very important to take account of impurities in calculating the results of the thermochemical

measurements. When this allowance is made, the product has the composition $Li_3N$, and the reaction $Li_3N + nH_2O$ liq. = 3LiOH diss. + $NH_3$ diss. develops +131·1 Cal., and hence 3Li sol. + N gas = $Li_3N$ sol. develops + 49·5 Cal. This value is lower than the heat of combination of lithium with hydrogen (+21·6 Cal. for Li), and, as a matter of fact, the nitride is decomposed somewhat easily when heated in hydrogen.

On the other hand, the hydride seems to be decomposed when heated in nitrogen, but what really happens is that the hydride dissociates and the nitrogen then combines with the liberated lithium.

C. H. B.

**Beryllium Oxide.** By PAUL LEBEAU (*Compt. rend.*, 1896, **123**, 818—821).—Pure beryllium oxide, prepared by the method previously described (Abstr., 1896, ii, 168), fuses in the electric arc, and, on cooling, forms a white, crystalline mass, slightly harder than rubies. On the surface, there are often small, detached hexagons, resulting from condensation of vapour of the oxide, which, therefore, is somewhat volatile in the arc. The sp. gr. of the oxide dried at 440° is 3·012 at 0°, and that of the fused oxide 3·025 at 0°; it follows, therefore, that no appreciable polymerisation takes place at a high temperature. The fused oxide is not attacked by gaseous hydracids at a red heat, but concentrated acids dissolve it slowly, and in this respect it differs from alumina. In sulphuric acid, it swells up and yields a dense crystalline powder of anhydrous beryllium sulphate, which dissolves very slowly in boiling water.

The oxide dried at 440° is attacked by fluorine when heated, but not by other halogens or by members of the sulphur and nitrogen groups. In the electric furnace, it is reduced by carbon, silicon, or boron and with the latter yields a crystallised boride mixed with carbon boride and a beryllium borocarbide. Potassium, sodium, and aluminium have no action on the oxide at high temperatures, and it is not reduced by magnesium, even at the boiling point of this metal.

C. H. B.

**Earths of the Yttria Group in Monazite Sands.** By PAUL SCHÜTZENBERGER and O. BOUDOUARD (*Compt. rend.*, 1896, **123**, 782—788. Compare Abstr., 1896, ii, 475).—The authors have fractionated the earths of the yttria group obtained from monazite sands, by means of fractional crystallisations of the sulphates and fractional decomposition of the nitrates. They find that after the former method has yielded an oxide of constant molecular weight, the latter allows it to be still further fractionated. Details of the fractionations are given; the extremes of the molecular weights of the oxides are 91·25 and 148, but both the extremes and all the intermediate fractions give the same spark spectrum, consisting chiefly of two bands at λ618—614, and λ602—595·5, with further bands at λ499—497·5 and λ481·5—480. These spectra seem to be identical with that of yttria, but the high equivalent of some of the fractions of oxides show that they are not identical with yttria.

C. H. B.

**The Alleged New Element, Lucium.** By WILLIAM CROOKES; (*Chem. News*, 1896, **74**, 259).—Careful physical and chemical examina-

tions, revealed the fact that P. Barriere's lucium was nothing but impure yttrium. D. A L.

**Reduction of Permanganic Acid by Manganese Dioxide.** By Harmon N. Morse (*Ber.*, 1897, **30**, 48—50. Compare Abstr., 1896, ii, 475).—The results already described (*loc. cit.*) are again enumerated (compare Hirtz and Meyer, this vol., ii, 93). In the spontaneous liberation of oxygen due to precipitated manganese dioxide, the author recognises a tendency to the production of substances forming a homologous series $MnO,5MnO_2$, $MnO,10MnO_2$, $MnO,15MnO_2$, differing by $5MnO_2$.

In presence of nitric acid, lead peroxide and permanganic acid both lose oxygen in accordance with the equation $2HMnO_4 + 3PbO_2 = H_2O + 2MnO_2 + 3PbO + 3O_2$. M. O. F.

**The Tempering of Steel in a Solution of Phenol.** By Levat (*Compt. rend.*, 1896, **123**, 945).—Steel tempered in a solution of phenol possesses greater hardness, elasticity, and flexibility than when tempered in water. A. C. C.

**Absorption of Nitric Oxide by Ferrous Bromide.** By Victor Thomas (*Compt. rend.*, 1896, **123**, 943—945).—The author has determined the amount of nitric oxide absorbed by known weights of ferrous bromide dissolved in known volumes of water at 10°, and at 15—16°. At the lower temperature, two experiments gave results agreeing with the formation of a compound of the formula $3Fe_2Br_4,4NO$. At the higher temperature, the absorption corresponded with the formation of a compound of the formula $Fe_2Br_4,NO$. These results are confirmatory of those obtained by Gay with ferrous sulphate and chloride, who found that, below 12·5°, 3 atoms of iron united with 2 molecules of nitric oxide, whilst above that temperature 2 atoms of the metal united with 1 molecule of the gas. In a future communication, the author will describe a crystalline compound obtained by the union of nitric oxide with ferrous bromide in ethereal solution.

A. C. C.

**Crystallised Magnesium Chromite.** By Em. Dufau (*Compt. rend.*, 1896, **123**, 886—888).—When a mixture of chromium sesquioxide (150 grams) and magnesium oxide (40 grams) is heated in the electric furnace with an arc of 50 volts and 300 ampères, normal magnesium chromite, $MgCr_2O_4$ is formed which can easily be obtained as a dark green, crystalline powder. The crystals, which are octahedral, have a sp. gr. = 4·6 at 20°, are harder than quartz, and have no action on polarised light. They are readily attacked by sulphuric acid, slowly by hydrochloric and hydrofluoric acids, and are not acted on by boiling nitric acid. Chlorine, bromine, iodine, and sulphur have no marked action on the compound, and it is oxidised only with great difficulty, even when heated to redness in oxygen or when fused with potassium chlorate or nitrate. Under the conditions of the experiment, no basic chromites were formed. A. C. C.

**Molybdenum Iodide.** By M. Guichard (*Compt. rend.*, 1896, **123**, 821—823).—When molybdenum chloride, obtained by the direct

action of chlorine on the metal, is heated in a current of hydrogen iodide, a considerable quantity of iodine is liberated and a brown, amorphous di-iodide, $MoI_2$, is formed, of sp. gr. 4·3; it is insoluble in water and alcohol. When heated in a vacuum up to the melting point of glass, it is not decomposed, but when heated in air, iodine is liberated and an oxide is formed which, at a higher temperature, is converted into molybdic anhydride. Hydrogen reduces the iodide at 500°, and the change is very rapid at an incipient red heat. Chlorine decomposes it below 240°, and bromine behaves similarly. In oxygen at 350°, there is vigorous incandescence, with liberation of iodine and formation of molybdic anhydride. Sulphur readily converts the iodide into a black sulphide, but nitrogen is without action at the softening point of glass. Water decomposes it very slightly at the ordinary temperature, and a little more rapidly at 700°, whilst in superheated steam, hydrogen is liberated as well as hydrogen iodide, probably as a result of the decomposition of the steam by an oxide, MoO, formed as the first product of the action of the steam on the iodide. Hydrogen sulphide converts the iodide into sulphide, and sulphuric and nitric acids oxidise it slowly in the cold and more rapidly on heating. Aqueous potash acts on it slowly at the ordinary temperature.

C. H. B.

## Mineralogical Chemistry.

**Artificial Pirssonite: Simultaneous Production of Northupite, Gaylussite, and Pirssonite.** By August B. de Schulten (*Compt. rend.*, 1896, **123**, 1023—1025).—Bright, limpid crystals of the new mineral, pirssonite (this vol., ii, 48), have been artificially produced by adding excess of calcium chloride to a solution of sodium carbonate and heating the mixture on the water bath for 12 hours. The minute crystals are orthorhombic, and are tabular parallel to *b* (010), but do not show the hemimorphism which is so characteristic of the natural mineral; they have the optical characters of pirssonite. The composition is $CaCO_3,Na_2CO_3,2H_2O$; sp. gr. 2·349. At 100°, there is no change, but at 130°, most of the water is lost. When placed in water, the crystals soon become dull, and after a time are decomposed into calcium and sodium carbonates.

The new mineral, northupite, has already been artificially prepared by the author (Abstr., 1896, ii, 610). Northupite, pirssonite, and gaylussite all occur together at Borax Lake, California, and they have been prepared simultaneously by heating for some hours on the water bath a mixture of 150 grams of sodium chloride, 50 grams of sodium carbonate, 6 grams of calcium chloride, and 10 grams of magnesium chloride in 550 c.c. of water. By this method, octahedra of northupite and delicate needles of gaylussite are obtained, and, as the solution is concentrated, pirssonite is formed at the expense of the gaylussite. Rhombohedral crystals of the double salt $MgCO_3,Na_2CO_3$ (Abstr., 1896, ii, 610) are also formed at the same time, and it is predicted that this will be found as a natural mineral at Borax Lake.

L. J. S.

**Anhydrite in Ontario.** By W. NICOL (*Canadian Record Sci.*, 1896, 7, 61).—Anhydrite occurs in considerable quantity at the Foxton phosphate mine, township of Loughborough, Co. Frontenac. It is associated with gypsum, calcite, and pyroxene, and resembles pink fluorite in appearance. Analysis gave

| CaO. | $SO_3$. | $CO_2$. | $SiO_2$. | $Fe_2O_3$. | Loss on ignition. | Total. |
|---|---|---|---|---|---|---|
| 41·71 | 57·47 | 0·286 | 0·151 | 0·065 | 0·26 | 99·942 |

L. J. S.

**Valleite, a new Orthorhombic Amphibole.** By GIUSEPPE CESÀRO (*Bull. Acad. Sci. Belg.*, 1896, [3], 32, 536—545. Compare Abstr., 1896, ii, 481).—This mineral occurs with the violet tremolite (hexagonite) of Edwards, St. Lawrence Co., N.Y.; it closely resembles anthophyllite in appearance, but differs from it in its optical characters and in containing only a small amount of iron. The indistinct crystals are flattened parallel to (100) and have a perfect lamellar cleavage in this direction; other cleavages are (010), (021), and, less distinct, (110), (011), (031), and (001). The prism angle is 54° 30′; $a:b:c = 0·515:1:0·255$. The plane of the optic axes is (010), and the acute negative bisectrix is perpendicular to (100); 2E = 90° 28′. H = 4·5; sp. gr. 2·88. It is easily fusible to a white, nearly opaque, bead. Analysis by Renard gave

| $SiO_2$. | MgO. | CaO. | $Fe_2O_3$. | MnO. | $K_2O$. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|---|
| 58·02 | 27·99 | 5·04 | 1·28 | 2·88 | 0·89 | 3·13 | 99·23 |

This agrees with the metasilicate formula, $RO,SiO_2$. L. J. S.

**The Garnet Group.** By H. SCHNERR (*Zeit. Kryst. Min.*, 1896, 27, 431—432; from *Inaug.-Diss.*, *München*, 1894).—Several analyses are given of the lime-garnets associated with the serpentine masses of the Eastern Alps; some of these have been quoted by Weinschenk (this vol., ii, 106). The following are of garnets from the Rothenkopf, Zillerthal, Tyrol: I, light red; II, cherry-red; III, dark brown.

| | $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MnO. | CaO. | Total. |
|---|---|---|---|---|---|---|---|
| I. | 37·18 | 14·03 | 13·73 | 2.54 | trace | 32·73 | 100·21 |
| II. | 36·75 | 6·90 | 21·38 | 2·17 | trace | 32·55 | 99·75 |
| III. | 37·52 | 13·29 | 13·01 | 1·71 | 0·54 | 34·01 | 100·08 |

As in the garnets of the Gross-Venediger, the dark brown shows the more marked optical anomalies, whilst the cherry-red is almost isotropic. From the analyses, it is seen that there is no connection between colour and chemical composition, and that the darker garnets (aplome) are not richer in ferric oxide than the lighter (essonite), as is sometimes supposed. L. J. S.

**[Action of Hydrochloric Acid on Titaniferous Augite.]** By E. LORD (*Zeits. Kryst. Min.*, 1896, 27, 431; from *Inaug.-Diss.*, *Heidelberg*, 1894).—In a dissertation on the basalts of the Fichtelgebirge the following analyses of the zoned titaniferous augite from the limburgite of the Kaiserstuhl, Baden, are given; these were made with the object of seeing whether, by the action of hydrochloric acid, a separation into parts containing titanium and free from titanium could be effected. The bulk analysis of the augite is given under I; II gives the com-

position of the portion (57 per cent. of the whole) which went into solution when the powdered mineral was digested for 12 hours with hot, concentrated hydrochloric acid; and III gives the composition of the insoluble portion.

| | $SiO_2$. | $TiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MgO. | CaO. | $Na_2O$. | $K_2O$. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|
| I. | 43·85 | 3·14 | 6·19 | 6·99 | 3·70 | 11·89 | 22·44 | 1.50 | 0·50 | 100·20 |
| II. | 43·41 | 3·19 | 6·92 | 7·04 | 3·38 | 11·64 | 22·54 | 1·50 | 0·50 | 100·12 |
| III. | 44·30 | 3·09 | 5·46 | 6·85 | 4·04 | 12·75 | 22·34 | [1·17] | | 100·00 |

After digesting for 4 days, 82·44 per cent. was dissolved; and with dilute acid (1 : 1), 43·77 was dissolved after 12 hours. In both these cases, the composition of the soluble and insoluble portions is, as before, much the same as that of the original augite, so that no separation can be effected by these means. L. J. S.

**Endomorphic Alterations of Granitic Magma in Contact with Limestone.** By ALFRED LACROIX (*Compt. rend.*, 1896, **123**, 1021—1023).—At the peak of Braceil, in Orlu, Ariège, the granite of Quérigut is in contact with a thick, sedimentary series consisting of schists with thick bands of limestone. Fragments of the schist and limestone are enclosed in the granite, and these rocks have been largely absorbed by the granitic magma. The granite in contact with the extensively corroded limestone has undergone considerable alterations; it becomes progressively more basic, by loss of quartz and felspar, and development of hornblende and mica, and lastly olivine, and passes to hornblende granite, quartz-diorite, mica-diorite, hornblendite, and, finally, to hornblende-peridotite, this being an almost complete series of granular eruptive rocks. Sometimes enstatite is developed, and norites, with or without olivine, result. The plagioclases, oligoclase to anorthite, are zoned and much corroded, indicating great variations in the composition of the magma. L. J. S.

**Gas from the Mineral Waters of Bagnoles de l'Orne.** By CH. BOUCHARD and ALEXANDRE DESGREZ (*Compt. rend.*, 1896, **123**, 969—970).—The gas from the mineral waters of Bagnoles de l'Orne contains carbonic anhydride, 5·0; nitrogen, 90·5; argon, 4·5; helium, traces = 100·00. No carbonic anhydride is found in the mineral waters of Cauterets. C. H. B.

**Mineral Water of Kralitz.** By FR. FAKTOR (*Verh. naturf. Ver., Brünn*, 1896 (1895), **34**, 366—368).—The baths of Kralitz, near Prossnitz, in Moravia, have been known since 1825. The water has a temperature of 9°; sp. gr. = 1·00544 at 16·5°; on standing, it becomes turbid, and deposits ferric oxide, silica, and organic matter. Analysis gave, in 1,000,000 parts:—FeO, 18·526; CaO, 158·400; MgO, 41·656; $K_2O$, 32·118; $Na_2O$, 44·961; $SiO_2$, 15·600; $SO_3$, 36·382; $P_2O_5$, 0·260; Cl, 50·763; $CO_2$, in bicarbonates, 330·110; $CO_2$, free, 9·073; total solids (dried at 180°), 562·029. L. J. S.

## Physiological Chemistry.

**Mercury Air Pump for the Estimation of Blood-Gases.** By FRIEDRICH NEESEN (*Zeit. physiol. Chem.*, 1896, **22**, 478—482).—This is a modification of the mercurial air pump, the details of which are fully explained, and illustrated by a diagram. The special advantage claimed for it is rapidity of action. W. D. H.

**Gastric Digestion.** By FERDINAND KLUG (*Pflüger's Archiv.*, 1896, **65**, 330—342).—A large number of albuminous substances were subjected to the action of gastric juice prepared from the dog, pig, and ox, and the results compared. Differences between the three juices occur; but the main result is that alkali-albumin and casein are best digested , after these follow serum-albumin, syntonin, serum-globulin, fibrin and legumin ; whilst boiled egg-albumin and dry meat powder are the least easily digestible. The yield of anti-albumose is greatest with alkali-albumin and plant-casein ; then follow serum-globulin, syntonin, serum-albumin, and casein. The yield of hemi-albumose is greatest with casein, both animal and vegetable ; serum-albumin, syntonin, gluten, and gluten-fibrin also yield a relatively large amount of hemi-albumose ; serum-globulin, fibrin, boiled egg-white, legumin, and raw flesh yield relatively little. On the other hand, serum-globulin and syntonin yield the most peptone ; egg-albumin, casein, serum-albumin, and fibrin follow in the order named.

Another series of tables gives the effects of different acids. The absolutely greatest quantity of proteid is dissolved by pepsin in the presence of hydrochloric and lactic acids ; phosphoric, nitric, acetic acids follow, and then, at a distance, sulphuric and citric acids. The optimum concentration differs with the different acids ; thus it is 0·6 for hydrochloric, 8·0 for lactic, 6·0 for phosphoric and acetic, 0·8 for nitric, 0·6 for sulphuric, and 8·0 for citric acid. The relative proportion of hemi- and anti-products differs considerably with the various acids, a fact which is against the supposition that the hemi- and anti-group exist preformed in the albuminous molecule. W. D. H.

**The Blood of New-born Animals.** By HUGO WINTERNITZ (*Zeit. pysiol. Chem.*, 1896, **22**, 449—477).—The blood of the fœtus, and of the new-born animal, is much richer in hæmoglobin and total solids than that of the adult animal, but shortly after birth this large proportion begins to diminish. The experiments recorded were made on dogs, cats, and rabbits, the hæmoglobin being estimated by the Hoppe-Seyler double pipette. W. D. H.

**A New Enzyme in the Blood.** By MAURICE HANRIOT (*Compt. rend.*, 1896, **123**, 753—755. Compare Abstr., 1892, 742).—The object of this investigation was to determine the manner in which reserve fat passes into the circulation and is utilised by the organism. In his experiments, the author, instead of employing the natural fats, makes use of an aqueous emulsion of monobutyrin as a test for the presence of a hydrolysing enzyme, on account of the greater ease with which

it is capable of undergoing saponification. Monobutyrin is readily saponified by blood serum in neutral or slightly alkaline solutions, but the action is considerably retarded by the presence of the liberated acid if this be left unneutralised. Using equal quantities of butyrin, the acidity in a given time is directly proportional to the amount of serum employed; moreover, the activity of the latter is destroyed when it is heated to 90°, it being then unable to produce butyric acid in the test solution. The amount of saponification taking place with various proportions of butyrin and serum in different times was determined by observing the quantity of a standard solution of sodium carbonate necessary to neutralise the liberated butyric acid; and the results are given in a table. The active enzyme, for which the name *lipase* is suggested, is also capable of acting, though much more slowly, on the natural oils and fats. *Lipase* is very stable, and appears to be as active in the serum at the end of eight days as at the beginning. In a future communication, the author proposes to show the invariable presence of lipase, both in plants and animals, whenever there is a reserve of fat to be utilised. A. C. C.

**Fat in the Blood during Hunger.** By Fr. N. Schulz (*Pflüger's Archiv.*, 1896, **65**, 299—307).—The experiments were made on rabbits, pigeons, and dogs. The fat was estimated by extraction with ether after preliminary artificial gastric digestion. Inanition was found to cause a rise of from 30 to 100 per cent. in the amount of fat in the blood, as compared with that in normal animals. W. D. H.

**Absorption of Fats.** By B. Moore and D. P. Rockwood (*J. Physiol.*, 1897, **21**, 58—84).—The emulsibility of free fatty acids, and their solubility in bile, have been known for many years, but the extent of such solubility has not been ascertained, and the bearing of these facts on fat absorption has not attracted much attention. The present research attacks both these points. In connection with the first, the solubility determinations show: (1) that palmitic and stearic acids are practically insoluble in ox bile at 38—40°, whilst 4 per cent. of oleic acid is easily soluble at that temperature. Hence the solubility of mixed fatty acids is probably due to an action of oleic acid in aiding the solution of the others. (2) Of the mixed fatty acids of lard, beef suet, and mutton suet, lard acids are most, and mutton suet acids least, soluble, the solubilities for the three sets being 3·5, 2·5, and 2 per cent. respectively in ox bile, 5, 5, and 1 in pig's bile; and 6, 5·5, and 2 in dog's bile. (3) The solubility of the fatty acids in bile is only in part due to bile-salts. Strong solutions of the bile-salts dissolve fatty acids much more feebly than the bile itself. Mere removal of the pseudomucin from bile diminishes its solvent action. A solution of pseudomucin alone, however, does not dissolve fatty acids. (4) On cooling the solution of fatty acids in bile below 40°, much of the dissolved acids separates out. The power of the bile to dissolve fatty acids is not impaired by repeating the process; the formation of a true emulsion was never observed.

The intestinal contents of the dog dissolve fatty acids in a way very similar to bile. Pancreatic juice and bile together decompose and dissolve fat; pancreatic juice alone decomposes, but does not

dissolve it, whilst bile alone has no action. A large number of experiments were made on the reaction of the intestinal contents in different animals, and the results and conclusions drawn therefrom may be summarised as follows.

The way in which fat is absorbed varies in different species of animals, and certainly it is not always absorbed as dissolved fatty acids. Most, however, if not all, of the fat is absorbed in soluble form by the epithelial cells, either as fatty acid or soap. When fatty acids are dissolved in bile or the mixed intestinal juices, the reaction of the solution is acid. Intestinal contents, therefore, which are alkaline to litmus cannot contain free fatty acids in solution. In white rats, the reaction is alkaline to litmus along nearly the whole small intestine, and usually the whole way, and, in the dog, the same is usually the case for the lower part of the ileum. Yet lacteals filled with white emulsion are seen proceeding from these parts. Here, probably, the fat is absorbed as soap.

In the greater part of the dog's small intestine, the reaction is acid to litmus, but alkaline to methyl-orange. The acidity to litmus is due to organic, probably dissolved fatty, acids, but the alkalinity to methyl-orange indicates that there is an excess of alkali above that required to combine with inorganic acids, and that this excess is combined with weak acids, probably with fatty acids in the form of soaps.

Munk objected to the view that any considerable amount of fat is absorbed as soap, on two grounds: (1) the acid reaction of the intestinal contents; (2) the enormous quantity of alkali which would be necessary to saponify all the fat in even an ordinary meal. The first objection falls to the ground when one considers that the acidity is due to organic acids; and the second may be met by the suggestion that a small amount of alkali could act as the mere carrier of an indefinitely large quantity of fat, provided that, in the splitting up of soap into fatty acid and alkali which occurs in the epithelial cells, the alkali makes its way, as is probable, back to the intestine, rather than into the blood-stream.

Histologists are unanimous that fat does not enter the epithelium in the particulate form of an emulsion; fat granules have never been observed in the striated border of these cells. Emulsification usually occurs, it is true, and this is obviously useful for the exposure of a large surface of fat to the action of the intestinal fluids; but fat absorption, as shown by the lacteals, proceeds alike whether any piece of gut contains emulsion or clear fluid. W. D. H.

**The Fat of Flesh.** By E. Bogdanoff (*Pflüger's Archiv.*, 1896, **65**, 81—89).—Dormeyer's discovery (Abstr., 1895, ii, 540), that simple extraction of muscular tissue with ether is not sufficient to remove all the fat, is confirmed. By prolonged extraction with ether after the removal of the fat which is easily removable, a fat is obtained characterised, like butter fat, by a high percentage of volatile fatty acids. From the result of microscopical examination of the muscular tissue, which had been treated with osmic acid at different stages after ether extraction, the conclusion is drawn that the second fat is a constituent of the muscle-plasma. W. D. H.

**Chemistry of Animal Fats.** By CARL AMTHOR and JULIUS ZINK (*Zeit. anal. Chem.*, 1897, **36**, 1—17).—The authors, having special facilities for obtaining genuine specimens of the fat of various wild and domesticated animals, have made numerous estimations of specific gravity, melting and solidifying points, iodine and saponification numbers, both of the fats themselves and of the fatty acids, as well as the Hehner and Reichert values, the acetyl number (according to Benedikt and Ulzer), and the free acidity when fresh and after a lapse of time. The animals selected were the elk, red deer, fallow deer, chamois, roebuck, badger, wild boar, dog, fox, wild and domestic cat, pine marten, pole cat, hare, tame and wild rabbit, tame and wild duck and goose, and the last, after two years' captivity, domestic fowl, turkey, black cock, dove, and starling. The first five are distinguished from the others by high specific gravity and low iodine number, the iodine number of chamois fat being the lowest yet recorded. The fat of the wild boar, hare, wild rabbit, and black cock exhibits the property of drying to a varnish when exposed to the air in a thin layer; the fat of the domestic pig and rabbit does not dry. Comparing the fat of wild with that of domestic animals, the former always shows a higher iodine absorption and generally a higher acidity in the fresh state; in the case of the wild goose kept in captivity for two years, the iodine number had fallen to that of the domestic goose. Besides the above numerical values, observations of colour, consistency, odour, &c., are recorded.

M. J. S.

**Muscular Work and Glycogen.** By FRIEDRICH SCHENCK (*Pflüger's Archiv.*, 1896, **65**, 326—328).—A further criticism of Seegen's work. (Comp Abstr., 1896, ii, 48).

W. D. H.

**Oxidation in the Tissues.** By AN. MEDVEDEFF (*Pflüger's Archiv.*, 1896, **65**, 249—277).—The principal experiments recorded were made with salicylaldehyde and extracts of animal organs. Under certain circumstances, the amount of oxidation is proportional to the square of the concentration of the oxidation ferment (or active proteid), and inversely proportional to the square root of the concentration of the salicylaldehyde. Physiological oxidation processes belong to the class of what Schmiedeberg terms 'synthetic oxidations.'

W. D. H.

**Influence of Calcium Salts on Fibrin Formation.** By OLOF HAMMARSTEN (*Zeit. physiol. Chem.*, 1896, **22**, 333—395).—A very complete and critical article on the recent theories that have been advanced concerning the part played by calcium salts in the process of blood-coagulation, the points of difference between the theorists being tested by carefully-devised experiments. The view of Alex. Schmidt, that calcium salts do not qualitatively act differently from other neutral salts like sodium chloride, is not correct. Schmidt admits that the calcium salts are quantitatively more active than other salts, but Arthus and Pagès are undoubtedly right in attributing to calcium salts a specific action; and the removal of such salts by the addition of alkali oxalates inhibits coagulation, because the plasma is thereby decalcified. The use of the term decalcification is not abso-

lutely correct, for the calcium which is in intimate union with fibrinogen is not influenced by the oxalate.

The question then arises what is the specific action of calcium salts? Are they of use in the formation of fibrin ferment, or do they act, as in the formation of casein in milk, by precipitating the proteid which has been subjected to the action of the ferment? The analogy drawn by Arthus between casein formation and fibrin formation only holds good in part, for calcium salts are not essential for the fermentative change of fibrinogen into fibrin; provided fibrin ferment is present in sufficient amount, fibrin is formed typically and abundantly from solutions of fibrinogen, whether calcium salts have been removed by an oxalate or not.

Pekelharing is right when he assumes that the specific action of calcium salts is in the genesis of fibrin ferment, or, to adopt a new nomenclature, in the change of prothrombin (zymogen or percursor of fibrin ferment) into thrombin (the ferment itself). Fibrin is certainly not a calcium compound of fibrinogen; both contain the same amount of calcium.

Lilienfeld's thrombin, a substance he considered he had split off from fibrinogen by the action of acids like acetic or nucleic acid, and which he further supposed combined with calcium to form fibrin, does not exist. It is nothing but fibrinogen itself partially precipitated by the acid employed. W. D. H.

NOTE BY ABSTRACTOR.—No reference is made in this paper to a preliminary note by E. A. Schäfer (*Proc. physiol. Soc.*, 1895, 18), who arrived at much the same results on most points. Ringer (*Practitioner*, **24**, 81) has also shown, in connection with cardiac muscle, that soluble oxalates do not produce absolute decalcification.

**Fate of Cholesterol in the Animal Organism.** By STANISLAS BONDZYŃSKI and V. HUMNICKI (*Zeit. physiol. Chem.*, 1896, **22**, 396—410).—In man, the cholesterol of the bile leaves the body in the fæces as a new substance *coprosterol*; this has the formula $C_{27}H_{48}O$, and from an examination of its derivatives (see this vol., i, 183), appears to be dihydrocholesterol. In dogs, cholesterol is found in the fæces as such. In horses, the material found is named *hippocoprosterol*, $C_{27}H_{54}O$, or $C_{27}H_{56}O$. W. D. H.

**Behaviour of Formanilide in the Animal Organism.** By FRIEDRICH KARL KLEINE (*Zeit. physiol. Chem.*, 1896, **22**, 327—332).—The urine of animals fed on a diet mixed with formanilide was examined; in dogs, small doses of the drug are almost entirely destroyed in the metabolic process; large doses lead to the appearance of orthohydroxycarbanil in the urine. This same substance was found by Jaffe after the administration of acetanilide. It is produced by oxidation and a subsequent loss of water,

$$C_6H_5{\cdot}NH{\cdot}COH + O_2 = OH{\cdot}C_6H_4{\cdot}NH{\cdot}COOH = C_6H_4{<}{\genfrac{}{}{0pt}{}{N}{O}}{>}C{\cdot}OH + H_2O.$$

In rabbits, the substance found in the urine is amidophenol.

W. D. H.

**Ingestion and Excretion of Iron in Health.** By RALPH STOCKMAN and E. D. W. GREIG (*J. Physiol*, 1897, 21, 55—57).—The iron meta-

bolism of the body, so far as regards intake and output, is extremely small, an examination of the ingesta and egesta in four series of observations made on three healthy adults showing in the first and fourth observations that the intake and output were almost equal, amounting to 6·2 and 6·3 milligrams in one case, and 3·5 and 3·7 milligrams in the other. In the other two series, the iron excreted on the three days of the analysis was much greater than the amount ingested, but at other times the balance must be reversed, or the equilibrium of health would not be maintained.

Concerning internal iron-metabolism, which must be considerable if blood corpuscles are broken down in such large numbers as is commonly supposed, little or nothing is known. The greater part of the iron is apparently not excreted, but retained in store by the liver for future use. W. D. H.

---

## Chemistry of Vegetable Physiology and Agriculture.

**Alcoholic Fermentation without Yeast Cells.** By EDUARD BUCHNER (*Ber.*, 1897, **30**, 117—124).—When brewery yeast, to which no starch has been added, is ground with quartz sand and kieselguhr, moistened with water and pressed, the liquid which is obtained has the power of producing the fermentation of sugar, although it appears to be quite free from yeast cells. It has a sp. gr. of 1·0416, contains about 10 per cent. of residue, and gelatinises when boiled. This liquid produces alcoholic fermentation in solutions of cane-sugar, maltose, glucose, and fructose, but does not ferment either lactose or mannitol. Fermentation continued in many cases for two weeks, even at the temperature of 0°, and was not stopped by filtration of the liquid through a Berkefeldt filter. Plate cultures showed that in some cases small numbers of micro-organisms were present, but yeast cells were in no case detected. The author gives the name *zymase* to the substance which produces the fermentation. This appears to be a proteid, since the fermentative power of the solution is practically destroyed when it is heated for an hour at 40—50° and the coagulated albumin filtered off. The dried precipitate produced by alcohol does not yield any ferment to water. A. H.

**Effect of Ammonium Nitrate on Aspergillus niger.** By CHARLES TANRET (*Compt. rend.*, 1896, **123**, 948—950).—When *Aspergillus niger* is sown in Raulin's solution, the spores germinate in less than 24 hours, forming a mycelium which soon produces black conidia. When, however, the ammonium nitrate in the nutrient solution is increased from 0·25 per cent. to 0·5 or 0·75 per cent., the spores, at a temperature of 30—40° produce a mycelium, which grows rapidly but does not fructify. At a temperature of 20—22°, even 1 gram of ammonium nitrate per 100 c.c. of solution does not prevent the formation of conidia. During the growth of the aspergillus in the mycelial state, both citric acid and nitric acid are formed in the solution, and

starch appears in the tissue of the mould. When grown in Raulin's solution, no starch is elaborated. A. C. C.

**Behaviour of Bacteria towards Chemical Re-agents.** By THEODOR PAUL and BERNHARD KRÖNIG (*Zeit. physikal. Chem.*, 1896, 21, 414—450).—In order to determine quantitatively the effects of various acids, bases, oxidising agents, and metallic salts on bacteria, the numbers of colonies were counted after similarly-prepared cultivations were treated with the respective compounds. The bacteria employed in the experiments were *Staphylococcus pyogenes aureus*, and the spores of the anthrax germ, *Bacillus anthracis*, and numerous experiments were performed with each compound examined. The authors obtained the following results. The salts of mercury, gold, and silver exert a specific poisonous effect, strongest in the case of the mercury compounds; platinum salts have little action, if any. In metallic salt solutions in which the metal is present as a complex ion, the disinfecting action is extremely small; it is, however, not only dependent on the number of the metallic ions, but also on the anion and the non-dissociated part. The effect of mercuric chloride is greatly decreased by the addition of sodium chloride, or other chlorides, but is not affected by other salts, such as sodium nitrate. The acids only act as disinfectants in concentrations of the gram molecular weight per litre, and exhibit a specific action which is not proportional to the concentration of the hydrogen ions. The weak organic acids, however, appear to act according to the degree of dissociation. Lithium, sodium, and potassium hydroxides have almost equal effects, but the action of ammonium hydroxide is very slight. Of the oxidising agents, nitric acid, chromic acid, chloric acid, and permanganic acid act in the order stated, which is also that of their oxidising powers as determined electrically (Abstr., 1893, ii, 58). The halogens have also a specific action, which is most powerful in the case of chlorine. Phenol acts better in a 5 per cent. solution than at higher concentrations, and the effect is increased by the addition of metallic salts, most noticeably sodium chloride; it is, however, diminished by dissolution in alcohol, and in the most favourable conditions is not nearly as great as that of mercuric chloride, which appears to be the strongest disinfectant examined. In absolute alcohol, however, even this compound, like other salts, has little or no effect, but acts best in a solution containing water and alcohol in proportions which vary with the different compounds. L. M. J.

**Chemistry of the Membranes of Lichens and of Fungi.** By F. ESCOMBE (*Zeit. physiol. Chem.*, 1896, 22, 288—306. Compare Winterstein, Abstr., 1894, ii, 425; 1895, i, 80, 199, 323, 493). The hyphen-membranes of *Cetraria islandica*, after the extraction of fats, oils, colouring matter, astringent substances, lichenin, &c., consists mainly of an insoluble anhydride of galactose, which the author terms *paragalactan*; on oxidation, it yields mucic acid. Lichenin on hydrolysis yields, apparently, only galactose (compare E. Fischer), and is, therefore, probably a galactan. No chitin, or related substance, and no cellulose could be detected. The membrane of *Peltigera canina* contains no cellulose, but apparently a small amount of chitin. *Evernia prunastre* was also investigated, the algæ cells contain cellulose, and the hyphen-membrane a substance which, on treatment with potassium

hydroxide, becomes gelatinous. A substance was obtained from the sclerotium of *Claviceps purpurea* which could not be identified.

J. J. S.

**Crystalline Nitrogenous Compounds in Seedlings.** By Ernst Schulze (*Zeit. physiol. Chem.*, 1896, **22**, 411—434. Compare Abstr., 1895, ii, 84).—Complete details for the isolation of the different amido-acids are given. Seedlings of *Picea excelsa*, grown in sand in a dark room, contain asparagine with a little glutamine, whilst in the open, in good soil, no asparagine, but a considerable amount of glutamine, can be obtained.

Etiolated seedlings of *Lupinus albus*, of $2\frac{1}{2}$ weeks' growth, yielded phenylalanine, amidovaleric acid, and asparagine, but apparently no leucine. Arginine could not be isolated from the cotyledons of the same seedlings. Normal green seedlings gave a quantity of leucine and amidovaleric acid, but only a little asparagine, and apparently no phenylalanine. Green seedlings of *Lupinus luteus* gave leucine, a small quantity of asparagine, and a fair amount of arganine.

Etiolated seedlings of *Lupinus angustifolius L.* yielded leucine and amidovaleric acid, and the presence of small quantities of phenylalanine and arginine was also indicated. J. J. S.

**Nitrogenous Compounds derived from the Proteid Substances of certain Conifers.** By Ernst Schulze (*Zeit. physiol. Chem.*, 1896, **22**, 435—448. Compare Abstr., 1895, ii, 84).—Etiolated seedlings of *Picea excelsa* contain arginine, together with smaller quantities of asparagine and glutamine; normal green seedlings, however, contain arginine and glutamine, but no asparagine. The seedlings of *Abies pectinata* contain even more arginine, but little or no glutamine and asparagine. Seedlings of *Pinus sylvestris* contain arginine and asparagine, with a little glutamine. J. J. S.

**Analyses of the Juice of Different Varieties of Gooseberries, Currants, and Strawberries.** By Albert Einecke (*Landw. Versuchs.-Stat.*, 1896, **48**, 131—160. Compare Abstr., 1895, ii, 366.)—The analyses include invert and cane-sugar, acid, extract, nitrogenous matter, crude ash, phosphoric acid, and potash. The sp. gr. of the juice was also determined. The results are given in percentages in the berries.

The variations in the amounts of important constituents in the different varieties are, as a rule, not considerable, and it is not at present possible to ascertain by analysis to what variety a sample belongs. Comparing the produce of 1894 and of the dry season of 1895, it was found that, whilst gooseberries were richer in juice in 1894, the currants contained more juice in 1895. The juice of both fruits was richer in constituents in 1895 than in 1894 (except nitrogen in currants). With regard to the influence of manures on the composition of the juice, no effect was observed in the case of gooseberries and currants. In the case of strawberries, there was an increase of valuable constituents under the influence of manure, whilst the percentage of nitrogen was lowered; of ash constituents the amount of potash was increased, whilst that of phosphoric acid was diminished, by manuring. N. H. J. M.

# Analytical Chemistry.

**Estimation of Sulphur in the Gases Produced by the Combustion of Petroleum.** By RICHARD KISSLING (*Chem. Zeit.*, 1896, 20, 199).—A small lamp, with a reservoir capable of holding about 100 grams of oil, is fitted with a lamp-glass made of hardened glass the top of which is drawn out and bent so that it may be connected with a series of absorbing tubes.

By means of a current of air, the products of combustion are first passed through a U-tube 200 mm. long filled with glass beads moistened with a 5 per cent. solution of potassium permanganate. The gases then again pass through a nitrogen bulb also filled with permanganate solution, and finally through an empty bulb. When the combustion is over, the tubes are rinsed, the liquid cleared by boiling with hydrochloric acid, and the sulphuric acid estimated with barium chloride in the usual manner. The air in the room should, of course, be free from any sulphurous vapours. L. DE K.

**Estimation of Ammoniacal Nitrogen in Artificial Manures.** By O. BÖTTCHER (*Chem. Zeit.*, 1896, 20, 151—152).—The author has proved by a large number of experiments that ammoniacal salts contained in manures are completely decomposed by boiling with water and calcined magnesia. Boiling with aqueous soda is, therefore, unnecessary, and is often the cause of finding too high a percentage of ammonia, due to decomposition of the nitrogenous organic matter.

The magnesia should, however, be free from carbonate—if not, the results will be untrustworthy. L. DE K.

**A New Method of Estimating Phosphorus in Phosphor-Bronze.** By FELIX OETTEL (*Chem. Zeit.*, 1896, 20, 19—20).—From 3 to 10 grams of the sample in turnings or filings is digested with nitric acid, and the oxide of tin collected, slightly washed, dried, and ignited in a porcelain crucible; it is then mixed with about thrice its weight of potassium cyanide and fused for a few minutes at a red heat. In this way, the oxide is reduced to metallic tin, and the melt contains, besides potassium cyanide and cyanate, all the phosphorus as potassium phosphate. The melt is boiled with water, filtered, the cyanogen compounds removed by boiling with hydrochloric acid, and the traces of tin or copper which have again passed into solution are precipitated by a current of hydrogen sulphide and the whole filtered. The filtrate is concentrated to a small bulk, the last traces of the hydrogen sulphide are decomposed by adding a little bromine water, and the phosphoric acid is finally precipitated by adding ammonia magnesium mixture. The test-analyses are satisfactory; the presence of arsenic does not interfere. L. DE K.

**Critical Examination of Methods for the Estimation of Phosphoric Acid.** By C. MEINEKE (*Chem. Zeit.*, 1896, 20, 108—113). —The author has long ago proposed to ignite the yellow phosphomolybdate precipitate before weighing it; the latest investigation shows that it contains 3·944 per cent. of phosphoric anhydride.

The precipitation of phosphoric acid by means of molybdate solu-

tion is not influenced by the presence of an excess of ammonium chloride.

The magnesium pyrophosphate obtained when the magnesium method of precipitating phosphoric acid is employed, is not the stable compound which it was formerly believed to be, but contains what may be regarded as free phosphoric acid, which volatilises at a very high temperature. The author thinks the precipitate should be first ignited in the ordinary way and then at a much stronger heat; the loss then observed represents the free acid. L. DE K.

**Estimation of Phosphorus in Coal Ash.** By LOUIS CAMPREDON (*Compt. rend.*, 1896, **123**, 1000—1003).—When very finely-powdered coal-ash is heated with concentrated hydrochloric acid for 15 or 20 hours, the whole of the phosphorus does not dissolve, and the proportion that remains in the residue is greater the higher the temperature to which the ash has been heated. It often amounts to 10 per cent., and may amount to as much as 25 per cent. of the total phosphorus present.

In order to get the whole of the phosphorus into solution, the ash must be heated with five times its weight of a mixture of equal parts of potassium and sodium carbonates. C. H. B.

**Estimation of Readily-Soluble Phosphoric Acid in Basic Slags.** By MAX GERLACH and MAX PASSON (*Chem. Zeit.*, 1896, **20**, 87—88).—The authors have shown that the active ingredient of Wagner's solution is the free citric acid, and that the large amount of ammonium citrate may be safely reduced to one-tenth. At a temperature of 17·5°, a 3 hours' treatment does not yield more soluble phosphoric acid than half-an-hour's extraction. This does not, however, imply that the undissolved phosphate is really insoluble; treatment with fresh quantities of solution will gradually dissolve it completely.

L. DE K.

**Phosphoric Acid: Estimation of Pyrophosphoric Acid.** By MARCELLIN P. E. BERTHELOT and GUSTAVE ANDRÉ (*Compt. rend.*, 1896, **123**, 773—776).—The method described is available in presence of orthophosphoric acid, but is not generally applicable in presence of metaphosphoric acid. The solution is precipitated with a mixture of magnesium chloride and ammonium chloride and acetate in presence of a considerable excess of acetic acid, and the liquid is heated on a water bath for 3 to 4 hours, in order to ensure complete precipitation. The pyrophosphate thus obtained contains a somewhat variable proportion of magnesium, and therefore it is washed, dissolved in dilute nitric acid, boiled for about an hour, and the orthophosphate into which it is converted is then precipitated in the usual way.

The magnesium pyrophosphate is comparatively stable, even when boiled with dilute acetic acid, but it is obvious that the boiling should not be too prolonged.

When orthophosphoric acid is also present, the filtrate from the precipitated pyrophosphate is concentrated and mixed with ammonia, which precipitates the phosphoric acid in the usual form.

C. H. B.

**Volumetric Estimation of Arsenic.** By EMERICH SZARVASY (*Ber.*, 1896, **29**, 2900—2902).—The arsenic is precipitated in the usual way as sulphide, the precipitate being collected by filtration through a plug of asbestos placed in a combustion tube. After being washed with alcohol and ether, and carefully dried in a current of warm air, it is heated in a stream of oxygen. The arsenious anhydride which condenses in the cold part of the tube is dissolved in aqueous soda, and estimated by means of iodine solution. A. H.

**Volumetric Estimation of Boric Acid.** By MAX HÖNIG and GUSTAV SPITZ (*Zeit. angw. Chem.*, 1896, 549—552).—The authors titrate the free acid with standard alkali in the presence of a sufficiency of glycerol, using phenolphthalein as indicator. As soon as the liquid turns red, more glycerol is added, and should this destroy the colour, more soda is run in. When dealing with borates or mixtures of the same with alkali carbonates, a little methyl-orange is first added and then a slight excess of hydrochloric acid. After boiling, using a reflux condenser, the liquid is cooled, carefully neutralised, and the boric acid estimated as directed above. Insoluble borates are boiled with excess of normal acid and then treated in the same way.

When the acid has to be estimated in the presence of silica—for instance, in enamels—the sample is fused with potassium sodium carbonate, the melt boiled with water, and the liquid mixed with ammonium chloride in quantity sufficient to nearly neutralise the alkali used. After boiling for some time, an ammoniacal solution of zinc oxide is added to complete the precipitation of the silica, and when the ammonia has been entirely driven off, the liquid is filtered and the precipitate washed with hot water. A drop of methyl-orange is next added to the filtrate, then a slight excess of normal hydrochloric acid, and after boiling the mixture is treated as before.

Another process worked out by the authors is based on the following principles. Native insoluble borates, when made into an impalpable powder, are completely decomposed by boiling with solution of sodium hydrogen carbonate, passing carbonic anhydride through the boiling liquid. The solution, which then contains sodium tetraborate, and, of course, also alkali carbonate, is mixed with ammonium nitrate, and the carbonic acid quantitatively precipitated by silver nitrate, without throwing down any boric acid. When the liquid is now mixed with excess of ammonium chloride and distilled in a current of steam, the distillate contains an amount of free ammonia equivalent to the sodium in the tetraborate. From the amount of soda, the quantity of boric acid can readily be calculated. The results obtained by the second method agree fairly well with those obtained by the first process.

L. DE K.

[NOTE BY ABSTRACTOR.]—The titration of boric acid by means of glycerol, alkali, and phenolphthalein has been described by Thomson (Abstr., 1894, ii, 28); 30 per cent. of glycerol by volume was found to be always sufficient.

**Estimation of Sodium Carbonate, Silicate, and Borate in Soap.** By WM. WALTKE (*Chem. Zeit.*, 1896, **20**, 20—21).—From

5 to 10 grams of the soap, previously cut up small, is treated with boiling alcohol, and the insoluble portion is dissolved in hot water, filtered, evaporated to dryness, and the residue dried until the weight is constant. In an aliquot part of this residue, the carbonic anhydride is estimated in a Geissler's apparatus, and from the result the amount of sodium carbonate is calculated. The remainder is then treated with hydrochloric acid and the silica separated in the usual manner; in the filtrate from the silica, the whole of the sodium is present as chloride. This is now estimated volumetrically, and from the total thus found, the amount corresponding with the silicate and carbonate of sodium is subtracted; from the difference, the amount of sodium present as borate can be calculated.

When the salts are present in fair proportions, the results obtained by the process are quite satisfactory. L. DE K.

**New Method of Estimating Potassium.** By PAUL LÖSCHE (*Chem. Zeit.*, 1896, **20**, 38—39. Reply by H. HAEFCKE, *ibid.*, 88—89).—This process is intended for the analysis of crude potassium compounds containing an approximately known amount of potassium. Fifty grams of the sample is boiled with 150 c.c. of water and 10 c.c. of strong hydrochloric acid, and, when cold, diluted to 200 c.c.; 10 c.c. of the filtrate is then mixed with a sufficiency of platinic chloride solution, evaporated to dryness, and the residue broken up and repeatedly extracted with 96 per cent. alcohol to remove any sodium platinochloride. The insoluble matter is collected on a weighed filter, dried at 120°, and then washed with a 10 per cent. solution of ammonium chloride at 30° to remove the sulphates; the ammonium chloride in turn is removed from the insoluble residue of potassium platinochloride by washing with alcohol, and the filter and constants dried at 120—130°. The test-analyses are satisfactory.

HAEFCKE sharply criticises the process, and does not hesitate to reject the method as being quite untrustworthy. L. DE K.

**Estimation of Potassium at the Stassfurt Works.** By ALBERT ATTERBERG (*Chem. Zeit.*, 1896, **20**, 131. By RUDOLF RUER, *ibid.*, 270, and by EMIL BAUER, *ibid.*, 270).—ATTERBERG states that the chemists at the Stassfurt potash works use a process which gives results sometimes 2 per cent. in excess of the truth, and attributes this to the incomplete washing of the precipitated platinochloride. This should not be put on to the filter until completely exhausted with alcohol in the dish, and should be well broken up with a glass rod.

RUER also complains about the process giving results which are too high, amounting to about $\frac{1}{2}$ a per cent., and proposes to lower the factor 0·3056 to 0·304 so as to counterbalance the error.

BAUER prefers to avoid the weighing on a filter, and to redissolve the precipitate in boiling water. The liquid is then evaporated in a weighed platinum dish, and the residue dried at 120°. L. DE K.

**Estimation of Potassium at the Works at Leopoldshall, Stassfurt.** By TIETJENS and APEL (*Chem. Zeit.*, 1896, **20**, 202—203).—The authors, in reply to Atterberg (preceding abstracts), suggest

that the difference in the percentage of potassium found may possibly be due to the samples having absorbed moisture. L. DE K.

**Estimation of Potassium as Potassium Platinochloride.** By HEINRICH PRECHT (*Chem. Zeit.*, 1896, **20**, 209).—A reply to Atterberg (preceding abstracts). The author recommends treating the platinochloride residue with commercial absolute alcohol instead of spirits of wine; contrary to theory, the sodium platinochloride is more readily soluble in the former liquid, whilst the potassium salt is practically insoluble. L. DE K.

**Analysis of Commercial Copper by Electrolysis.** By A. HOLLARD (*Compt. rend.*, 1896, **123**, 1003—1005).—Ten grams of the copper is placed in water and 15 c.c. of concentrated sulphuric acid, and 40 c.c. of nitric acid of 36° B is added. Towards the close of the reaction, the liquid is gently heated. Antimony sometimes separates, but, if the quantity is small, it does not interfere with the estimation of the copper; if large, it is separated by filtration, dissolved in aqua regia containing a high proportion of nitric acid, evaporated to dryness, dissolved in dilute hydrochloric acid containing tartaric acid, and added subsequently to the liquid from which the copper has been removed, and in which the antimony is to be estimated.

The copper solution is diluted to about 350 c.c., Luckow's electrodes (cone and spiral) are introduced, the base of the spiral being about 6 mm. below the base of the cone, which should be completely covered by the liquid, and a current of about 0·3 ampère is allowed to pass until all the copper is precipitated. The firmly adherent deposit on the cone contains the copper and the silver. Part, but not all, of any lead that may be present will be deposited on the spiral as peroxide.

When more or less than 10 grams of copper is taken, the best quantities of sulphuric and nitric acid respectively are, for 1 gram, 1 c.c. and 30 c.c.; for 3 grams, 6 c.c. and 33 c.c.; for 5 grams, 10 c.c. and 35 c.c.; for 20 grams, 20 c.c. and 60 c.c.

The estimations of the other constituents of the copper will be described subsequently. C. H. B.

**Nessler's Reaction as a Test for Mercury or Iodides.** By GEORGES DENIGÈS (*Chem. Zeit.*, 1896, **20**, 70).—*Detection of Mercury.* The solution, measuring about 2 c.c., is mixed with 2 c.c. of ammonia, and potassium iodide is added in quantity just sufficient to redissolve the precipitate. On adding aqueous potash, the characteristic brown colour will appear.

*Detection of Iodine.*—The solution is, if necessary, precipitated with ammonium sulphide, and the filtrate boiled to expel the excess of the reagent. Ammonia and aqueous soda are first added to it, and then a solution of mercuric chloride, when the well-known coloration will be produced. L. DE K.

**Estimation of Mercury Salts by means of Sodium Dioxide.** By M. C. SCHUYTEN (*Chem. Zeit.*, 1896, **20**, 239).—The process is based on the remarkable fact that sodium dioxide, which possesses such strong oxidising properties, is yet capable of reducing mercury compounds to the metallic state.

The mercury compound, soluble or insoluble, is mixed with a sufficiency of water contained in a porcelain basin fitted with an inverted funnel, the stem of which is bent at right angles. Sodium dioxide is introduced in small portions at a time, as long as a precipitate is formed, and after putting on the funnel the whole is gently heated until vapours begin to condense in the neck of the funnel. When cold, the funnel is rinsed, and the metallic mercury is collected on a weighed filter, and dried in a desiccator. The process is not applicable to the native sulphide. L. DE K.

**Estimation of Thorium in Thorite.** By ERNST HINTZ and HERMANN WEBER (*Zeit. anal. Chem.*, 1897, **36**, 27—31).—The separation of thoria from the oxides of the cerium and yttrium metals is based on the solubility of thorium oxalate in ammonium oxalate, and its reprecipitation from this solution on the addition of hydrochloric acid. In opposition to Glaser (*Chem. Zeit.*, 1896, **20**, 613), the authors find that thorium oxalate dissolved in a hot concentrated solution of ammonium oxalate is not precipitated on diluting and cooling. The hydrochloric acid solution of 1 gram of the substance, freed from silica by evaporation, and from heavy metals by hydrogen sulphide, is diluted to 200 c.c. and precipitated hot by 1 gram of oxalic acid. After remaining for two days, the precipitate is collected, washed, and digested for several hours on the water bath with 60 c.c. of a solution (saturated cold) of ammonium oxalate. The mixture is diluted to 300 c.c., and allowed to remain cold for two days, then filtered, and the filtrate heated with 5 c.c. of concentrated hydrochloric acid, whereby the thorium oxalate is completely precipitated. The residue left undissolved by the ammonium oxalate is repeatedly digested with fresh portions of oxalate solution, and the filtrates treated as before. The thorium oxalate is then washed and ignited. It is, however, not yet quite free from cerium and yttrium. It is therefore redissolved, either by boiling with hydrochloric acid or by fusion with potassium hydrogen sulphate, precipitated with ammonia, dissolved in hydrochloric acid, and, after evaporation to expel excess of acid, its feebly acidified solution (diluted to 300 c.c.) is boiled with 3—4 grams of thiosulphate. The filtrate is precipitated by ammonia, the washed precipitate dissolved in hydrochloric acid, the solution evaporated, then taken up with a little water, and the boiling solution treated with a hot concentrated solution of ammonium oxalate. Water is added, and the mixture allowed to remain long in the cold. The precipitate consists of the oxalates of the cerium and yttrium metals, and the weight of the oxides is deducted from that of the impure thoria.

In some cases of very impure thorites, it is necessary to ignite the oxalates left undissolved by ammonium oxalate, and, after bringing them into solution as chlorides in feebly acidified water, to apply the thiosulphate method for the precipitation of the thoria present; but as the precipitation of thoria by this means is imperfect, the filtrate also requires to be treated by the ammonium oxalate separation method. (Compare Abstr., 1896, ii, 677.) M. J. S.

**Use of Nitroso-β-Naphthol in Inorganic Analysis.** By ROBERT BURGASS (*Zeit. angw. Chem.*, 1896, 596—601).—This reagent, first intro-

duced by von Knorre for the separation of cobalt and nickel (Abstr., 1893, ii, 500), has been tried by the author for the separation of other metals. He finds that copper, cobalt, and iron are completely precipitated; silver, tin, bismuth but partially, and these should, therefore, be removed before adding the nitrosonaphthol. Mercury, nickel, chromium, manganese, lead, zinc, aluminium, cadmium, magnesium, calcium, beryllium, antimony, and arsenic remain in solution.

In presence of excess of iron, any phosphoric acid will also be carried down; molybdic or titanic acid interferes with the accurate estimation of the cobalt or copper. L. DE K.

**Assay of Chrome Yellow and Chrome Red.** By HUGO AMSEL (*Zeit. angw. Chem.*, 1896, 613—618).—The author thinks that, if the sample is free from the carbonates and sulphates of barium, calcium, and lead, it may be passed as commercially pure. If a quantitative analysis has to be made, the best plan is to boil about 0·5 gram of the compound with a 10 per cent. solution of aqueous potash for some time; hydrochloric or nitric acid is then added in slight excess, and any insoluble matter, such as barium sulphate, is collected and weighed.

The filtrate is mixed with excess of sodium carbonate, and heated, with addition of bromine; the precipitate contains calcium carbonate and lead carbonate (the latter being partially converted into dioxide), whilst the filtrate contains sodium chromate and sulphate. The details present no novel features. L. DE K.

**Separation of Tungsten and Titanium.** By ED. DEFACQZ (*Compt. rend.*, 1896, **123**, 823—824).—A mixture of 8 parts of potassium nitrate and 2 parts of potassium carbonate, heated at its melting point, completely dissolves tungstic anhydride in 8 or 10 minutes, whether the anhydride has previously been strongly heated or not. Metallic tungsten is likewise dissolved. On the other hand, the fused mixture does not dissolve either titanium oxide or metallic titanium.

The substance to be analysed is heated to dull redness for 20 to 30 minutes with 7 to 8 times its weight of the mixture of nitrate and carbonate specified, and, after cooling, the product is treated with water and evaporated to dryness. The residue is first extracted with water and then washed with water containing ammonium nitrate, in order to prevent the titanium oxide from passing through the filter. The insoluble residue is dried, strongly heated, and afterwards fused with potassium hydrogen sulphate, the titanium being estimated in the usual way.

The tungsten in the solution is precipitated as mercurous tungstate. C. H. B.

**Commercial Prussian Blue.** By ERNEST J. PARRY and JOHN HENRY COSTE (*Analyst*, 1896, **21**, 225—230).—The authors have examined a large number of samples of commercial Prussian blue, and tabulated the results.

The chief point in the analysis is the estimation of the total iron, and the nitrogen; the latter by Kjeldahl's process. The factors for converting these into Prussian blue are respectively 3·03 and 4·4. In properly manufactured samples, the results obtained from these estimations ought to agree, but there may be occasionally either excess of iron or of nitrogen in the form of alkali or even of aluminium

ferrocyanide. Commercial blue may be passed as sufficiently pure if it contains 30 per cent of total iron and 20 per cent. of nitrogen. When boiled with sulphuric acid, it should become colourless in a few minutes without any charring. L. DE K.

**Analysis of "Cap Composition."** By F. W. JONES and F. A. WILLCOX (*Chem. News*, 1896, **74**, 283).—The method is based on the solubility of mercury fulminate in acetone saturated with gaseous ammonia. A tared filter paper is placed in a funnel to the neck of which has been fitted a piece of rubber tubing provided with a clip. The paper is moistened with a solution of ammonia in acetone; the finely-powdered cap composition is weighed off directly on to the filter paper, covered with the solution of ammonia in acetone, and the whole allowed to remain for 3 or 4 hours. It is then washed repeatedly with the same solution until the washings give no coloration with ammonium sulphide, and afterwards washed with acetone until the washings give no residue on evaporation; it is then dried, and weighed; the loss gives the amount of mercury fulminate. The paper and contents are again put in the funnel, washed with water until free from potassium chlorate, dried, and weighed; the further loss in weight gives the amount of potassium chlorate, and by deducting the weight of the filter paper from the last weighing, the amount of the antimony sulphide is obtained. D. A. L.

**Molybdic Acid, a Reagent for Alcohol.** By C. EMANUEL MERCK (*Chem. Zeit.*, 1896, **20**, 228).—By means of molybdic acid, it is possible to detect the presence of 0·2 per cent. of methylic alcohol, or 0·02 per cent. of ethylic alcohol, in the absence, of course, of any organic matter capable of interfering with the test. This is best carried out by dissolving molybdic acid in sulphuric acid at 60°, and pouring the hot solution gently into the liquid to be tested, when a blue ring will form at the surface of contact. On shaking, the colour disappears, but returns on adding more of the reagent.

L. DE K.

**Estimation of Alcohol by Means of the Ebullioscope; Influence of Extractive Matters.** By FRANZ FREYER (*Zeit. angw. Chem.*, 1896, 654—659).—The principle of the instrument (of which there are several varieties) is based on the difference between the boiling point of pure water and that of the spirit to be tested; a table is then referred to for the alcoholic strength of the sample.

The author points out that in the presence of much extractive matter the results are untrustworthy, as the alcohol may then be found several per cents. too high. A new table allowing for extractive matter is given. L. DE K.

**Detection of Caramel in Wine, and its Possible Confusion with Coal-tar Colours.** By A. J. DA CRUZ MAGALHAÊS (*Compt. rend.*, 1896, **123**, 896—897).—A sample of port wine examined by the author gave reactions pointing to the presence of a coal-tar colouring matter, although it was known that only caramel made from cane-sugar had been added. Further exeriments showed that caramel prepared from cane-sugar differs considerably from caramel made from

glucose, in that it behaves with certain reagents exactly like a coal-tar colour. Thus, when treated with basic lead acetate and then shaken with amylic alcohol, the former caramel communicated an orange-yellow colour to the solvent, whilst with the glucose caramel no coloration occurred. Ether, when shaken with a solution of the former, acquired an orange yellow colour, whilst with the latter no colour was extracted. Mordanted wool was dyed orange by the former, yellow by the latter. Genuine wine, to which no caramel had been added, did not give these reactions. A. C. C.

**Simple and Convenient Extraction Apparatus for the Analysis of Food Stuffs.** By J. L. BEESON (*J. Amer. Chem. Soc.*, 1896, 18, 744—745).—A modification of the Johnston extractor. The extraction tube, which is rather short, has a funnel stopper, and is so constructed that the sample may be weighed and dried in the same before extraction. After placing the tube in a Stutzer tube, the extraction with ether, &c., proceeds as usual, the returning drops of liquid being allowed to fall through the funnel tube on to the centre of the sample, so as to avoid loss of the latter. L. DE K.

**Reformation of the Present Methods of Analysis of Food Stuffs.** By F. JOSEF KÖNIG (*Landw. Versuchs.-Stat.*, 1896, 48, 81—110). —Owing to the probable difference in nutritive value of the pentosans and hexosans, it is desirable, if possible, to estimate separately the amounts of these two groups in food stuffs.

Experiments were first made in which rye grain and straw, and pea corn and straw, were treated with 1·25 per cent. sulphuric acid and 1·25 per cent. caustic potash. Both solutions dissolved more or less of the pentosans, and even 0·3 per cent. potash dissolved some, but in no case was the solution complete.

Superheated water dissolved the pentosans in rye flour and straw almost completely as well as the starch. When, therefore, starch is estimated by first dissolving with superheated water and subsequent inversion, results are obtained which are more or less too high, since the dissolved pentosans reduce Fehling's solution as well as the hexoses. To obtain more correct results for starch, it is therefore proposed (when superheated water is employed) to ferment the inverted solution with beer-yeast, and to estimate the carbonic anhydride or the alcohol produced. The method is, however, not perfect, owing to the production of hexoses from the cell-membrane. Pentosans seem to accompany the hexosans in all parts of plants. The following amounts of pentosans were found in starch from different sources: potato-starch, 1·25; maize-starch, 2·04; rice-starch, 1·40, and wheat-starch, 1·05 per cent.

Estimation of starch as maltose after treatment with diastase gave results which were too high, although less of the pentosans was dissolved than when superheated water was employed. The fermentation method would give better results.

The usual process of food stuff analysis has two faults, the use of too dilute acid and the use of too strong alkali. The acid is not strong enough to dissolve all the hemicellulose, whilst the alkali dissolves, besides fat and proteids, lignin, which should be either determined along with cellulose or else separately. With regard to alkali, it was

found that 0·5 per cent. soda solution dissolved almost the whole of the nitrogenous matter of the food, leaving a residue of crude fibre containing much the same amount of nitrogen as when 1·25 per cent. potash was used. The use of the more dilute alkali has the advantage that the lignin present is less attacked, and may therefore be estimated separately.

Experiments with different strengths of acid are still in progress, but the results so far obtained indicate that, whilst less than 12 per cent. hydrochloric acid is insufficient to dissolve the whole of the pentosans, better results may be obtained by heating under pressure with more dilute acid. N. H. J. M.

**Formaldehyde as a Reducing Agent. Estimation of Formaldehyde.** By BRUNO GRÜTZNER (*Arch. Pharm.*, 1896, **234**, 634—640).—To estimate potassium chlorate, the aqueous solution (about 2 per cent.) may be mixed with formalin (35 per cent. aqueous solution of formaldehyde—5 grams) nitric acid (5 c.c.; strength not named) and excess of silver nitrate solution. The mixture is heated on the water bath for half-an-hour, and the precipitated silver chloride then estimated by any of the usual methods.

Potassium bromate may be estimated on precisely similar lines, save that the heating must be continued for 2—2½ hours in order to complete the action. Iodates are not reduced by this method, and perchlorates only partially; periodates are reduced to iodates.

By mixing a measured volume of a formalin solution with an excess of potassium chlorate, adding a measured excess of N/10 silver nitrate solution, heating the mixture in the water bath until further heating produces no turbidity in the clear liquid above the settled precipitate, and titrating the excess of silver nitrate solution with potassium thiocyanate in the usual manner, the strength of the formalin solution may be determined. One molecule of silver nitrate corresponds with three of formaldehyde. A. G. B.

**Estimation of Formaldehyde.** By GYSBERT ROMIJN (*Zeit. anal. Chem.*, 1897, **36**, 18—24).—Besides reviewing the methods of Legler (Abstr., 1883, 1035) and of Brochet and Cambier (Abstr., 1895, i, 325) the author proposes two new ones, the first depending on oxidation by iodine in alkaline solution, and the second on the combination of formaldehyde with potassium cyanide, and he has studied their suitability for estimating formaldehyde both when occurring alone and when mixed with other substances of an aldehydic character, such as acetaldehyde, acetone, and benzaldehyde. A solution of formalin was used for the experiments. With the pure substance, all four methods gave practically identical results (37·38—37·9 per cent.), but owing to the want of sensitiveness of litmus in solutions containing hexamethylenetetramine, Legler's method requires the use of much stronger solutions than the other three, and is altogether of inferior accuracy.

The operations in the new methods are as follows. To a quantity of the solution containing about 15 milligrams of formaldehyde, there is added 25 c.c. of a N/10 iodine solution, and so much strong soda solution that the mixture becomes pale yellow. After 10 minutes, a small excess of hydrochloric acid is added, and the free iodine is titrated

with thiosulphate. Two atoms of iodine are consumed by 1 molecule of formaldehyde. With the pure substance, the results are perfectly concordant, and the great convenience of the method renders it the most advantageous of the four. It cannot, however, be used in the presence of the other aldehydes, and in the case of acetone, which, as shown by Krämer and Messinger, forms iodoform with quantitative completeness, the two substances are estimated jointly.

The reaction with potassium cyanide consists in the combination of the two substances in molecular proportion. Somewhat more than this amount of cyanide (in a solution containing about 6 grams per litre) is therefore added, and the mixture is poured into an excess of a N/10 solution of silver nitrate containing so much free nitric acid that the mixture remains acid. The excess of cyanide separates as silver cyanide, and the unprecipitated silver is titrated with ammonium thiocyanate (Volhard's process). In the presence of acetaldehyde, the aldehydecyanide mixture must be immediately added to the silver nitrate or the results obtained will be too high, but acetone and benzaldehyde are without influence, even if half-an-hour elapses at this stage. Legler's method seems not to be affected by the presence of the above three foreign substances, but the hydroxylamine method cannot be used in presence of any of them. M. J. S.

**Polarimetric Estimation of Tartaric Acid.** By Albert Colson (*Bull. Chim. Soc.* [ 3 ], **15**, 158).—The author experimented with solutions of tartaric acid of different strengths, made just alkaline with ethylenediamine. In the absence of impurities, and for solutions containing not more than 100 grams of tartaric acid per litre, the concentration could be directly determined from the observed rotation. In the presence of a substance such as citric acid, it was found that an error was introduced which increased with the amount of the second substance present. The observations could, however, be corrected by means of an empirical equation involving the density of a solution containing the same amount of ethylenediamine tartarate, and the density of the solution under observation. M. W. T.

**Estimation of Fat in Milk.** By Heinrich Fresenius (*Zeit. anal. Chem.*, 1897, **36**, 31—32).—The author, having made numerous comparisons of the methods of Gerber and Babcock (Abstr., 1891, 508) with the gravimetric process of extracting the milk, previously dried on sand, by ether, and weighing the residue obtained from the ethereal extract, finds that the results of the three methods agree satisfactorily. Gerber's process consists in mixing 10 c.c. of sulphuric acid (sp. gr. 1·82—1·83) with 1 c.c. of amylic alcohol and adding 11 c.c. of the milk. The flask is then closed by a caoutchouc stopper, well shaken, and then revolved for 3 minutes in Gerber's centrifugal machine. The fat collects in a graduated portion of the special-shaped vessel, and the reading gives the percentage at once. M. J. S.

**Method of Establishing the Purity of Butter by Determining the Specific Gravity.** By Raoul Brullé (*Bied. Centr.*, 1896, **25**, 638; from *Milchzeit.*, 1896, 297, and *Journ. Agric.*, 7 March, 1896).—The failure of sp. gr. determinations of butter fat as a means

of ascertaining the purity of butter, is attributed to the presence o water, colouring matter, &c. The following method is recommended for obtaining the fat in a pure state. The butter (100—500 grams) is melted, the fat separated as far as possible, violently shaken for some minutes with finely powdered calcium chloride (5—6 per cent.) and powdered animal charcoal (4 per cent.), and filtered. The fat, which is now colourless and quite dry, has a sp. gr. of 0·8655 at 100°, whilst oleomargarin has a sp. gr. = 0·8600, and the addition of 10 per cent. of margarin lowers the sp. gr. of butter fat by 0·00055.

N. H. J. M.

**Separation of Trimethylamine from Ammonia.** By Hermann Fleck (*J. Amer. Chem. Soc.*, 1896, **18**, 670—672).—The mixed hydrochlorides are repeatedly extracted with boiling absolute alcohol, which is then distilled off in a 750 c.c. distilling flask. Excess of aqueous soda is added to the residue, and the gases given off on boiling are passed into a large volume of water; litmus is added, and the liquid is neutralised exactly with dilute sulphuric acid. The whole is now evaporated to dryness, and the residue extracted with 1 litre of cold, absolute alcohol, which dissolves the trimethylamine sulphate, leaving the ammonium compound undissolved. The alcohol is distilled off, and the residue transferred to a weighed dish and dried until the weight is constant.

L. de K.

**Colour Reactions of Brucine; Detection of Nitrites in Presence of Sulphites.** By P. Pichard (*Compt. rend.*, 1896, **123**, 590—592).—Brucine in presence of hydrochloric acid and a trace of a nitrite yields, in 5 minutes or less, a vermilion red coloration which changes to pale yellow; this reaction is capable of detecting 1 part of nitrous acid in 640,000 parts of water. A nitrate under the same conditions gives no coloration. Chlorine and hypochlorous acid give no coloration with free brucine, but an intense vermilion coloration with the nitrate, chloride, acetate, and sulphate, especially the latter.

The presence of sulphites or sulphurous acid very materially reduces the sensitiveness and accuracy of the ordinary reactions for the detection and estimation of nitrous acid, and hence they cannot well be applied to soils which have been treated with calcium sulphate, and may in consequence contain lower sulphur compounds; this applies also, of course, to water that has percolated through such soils. On the other hand, the presence of 1 part of sulphurous acid in 2060 parts of water reduces the sensitiveness of the brucine test only to one-half, so that 1 part of nitrous acid in 329,000 parts of water can still be detected. This reaction should be used for the detection of nitrites in soils or drainage waters which may also contain sulphites. In either case, sulphides must first be removed if they are present; this is best done by agitating the solution with finely divided lead sulphate.

C. H. B.

**Testing Quinine Sulphate.** By Melchior Kubli (*Arch. Pharm.*, 1896, **234**, 570—585).—A reply to O. Hesse (Abstr., 1896, ii, 550).

A. G. B.

# General and Physical Chemistry.

**Optical Activity of Aspartic Acid in Aqueous Solutions.** By Ellen P. Cook (*Ber.*, 1897, **30**, 294—297).—It is well known that aspartic acid is dextrorotatory in all solutions to which acids have been added, but lævorotatory in those which contain alkalis. Investigators, however, differ as to the rotation of aqueous solutions of the pure acid. The author finds that a solution of the acid containing 1·872 parts of aspartic acid in 100 is dextrorotatory below 75°, but lævorotatory above that temperature. The addition of a single drop of aqueous caustic soda renders the solution lævorotatory, even at 20°.

The following are the values obtained.

| Grams of Aspartic Acid in 100 c.c. of Solution. | Temp. | Specific Rotation. $[\alpha]_D$. |
|---|---|---|
| 0·531 | 20° | +4·36 |
| 1·880 | 32 | +3·78 |
| 1·875 | 40 | +3·04 |
| 1·873 | 50 | +1·55 |
| 1·857 | 60 | +1·22 |
| 1·838 | 75 | 0 |
| 1·835 | 77 | −0·61 |
| 1·830 | 80 | −0·76 |
| 1·825 | 90 | −1·86 |

A. H.

**Selenic Anhydride.** By René Metzner (*Compt. rend.*, 1896, **123**, 1061—1063).—In a previous paper (this vol., ii, 132), the author has shown that the heats of combination of hydrogen selenate with one molecule of water (+9·1 Cal.) and of dissolution of the same acid (+16·8 Cal.) were approximately equal to the corresponding numbers for hydrogen sulphate. Assuming that the analogy holds good for the heats of combination of the anhydrides with one molecule of water, this number would be +19·6 Cal. for selenic acid, from which +42·1 Cal. is deduced as the heat of formation of selenic anhydride, a number which is smaller than the heat of formation of selenious anhydride from its elements. The endothermic nature of the formation of selenic anhydride from selenious anhydride and oxygen explains the failure of the attempts made hitherto to isolate it, as well as the ready formation of selenious anhydride and oxygen, when hydrogen selenate is heated with phosphoric anhydride under reduced pressure at 210—220°. This is also confirmed by a comparison of the two following thermic equations.

$$SeO_2 + O + H_2O = H_2SeO_4 \text{ liq.} \quad +3{\cdot}06 \text{ Cal.}$$
$$SO_2 + O + H_2O = H_2SO_4 \text{ ,,} \quad +56{\cdot}4 \text{ ,,}$$

A. C. C.

**Automatic Cut-off of Gas on Stoppage of the Water Supply.** By Hugo Michaelis (*Ber.*, 1897, **30**, 282—284).—The author

describes a simple apparatus by means of which the gas supply to burners which are employed for heating water baths, &c., may be automatically shut off when the water supply is by any accident stopped. A tap is inserted in the gas supply pipe, and is attached to a balanced lever, one arm of which carries a funnel through which the water supply has to pass. So long as this funnel is full, or overflowing, the lever remains horizontal and the gas tap is open, but as soon as the water supply ceases, the funnel empties itself through a small hole at the apex, the counterpoise falls, and the gas tap is closed. A. H.

**Apparatus for Filtering and Drying Substances Unstable in presence of Air.** By TASSILLY (*Bull. Soc. Chim.*, 1896, [3], **15**, 274—275).—The apparatus consists mainly of two filtering funnels, ground to fit tightly one on the other. Hydrogen, or some other inactive gas, is passed into the apparatus through the tube of the top funnel. M. W. T.

---

## Inorganic Chemistry.

---

**Structural Isomerism in Inorganic Compounds.** By ALEXANDER P. SABANÉEFF (*Ber.*, 1897, **30**, 285—287).—*Hydroxylamine hypophosphite*, $NH_3O,H_3PO_2$ can be obtained by the action of hydroxylamine sulphate on barium hypophosphite in an atmosphere of carbonic anhydride. Decomposition occurs when the solution is heated on the water bath, but, on spontaneous evaporation, needle-shaped crystals of the salt are deposited. It is hygroscopic, and melts at about 92°, occasionally exploding when heated. In dilute solution, it appears to be largely dissociated into its ions. This salt is isomeric (metameric) with ammonium dihydrogen phosphite (Amat, Abstr., 1888, 107), which melts at 123° and forms monosymmetric crystals.

The author claims this as the first well-defined instance of structural isomerism among inorganic compounds, and proposes to further investigate the metameric salts of the nitrogen bases. A. H.

*Note.*—The isomeric sodium potassium sulphites (Röhrig, *J. pr. Chem.*, [2], **37**, 217) and thiosulphates (Schwicker, Abstr., 1889, 942) are also instances of structurally isomeric inorganic compounds. A. H.

**Combustion of Coal Gas in Gas Engines.** By FRITZ HABER and A. WEBER (*Ber.*, 1897, **30**, 145—151).—The authors have examined the spent gases obtained from two varieties of gas engine. When working at full pressure, no appreciable amount of inflammable gas escapes, the product consisting, for the most part, of carbonic anhydride; at half-pressure, however, a considerable amount of an inflammable gas is evolved, consisting largely of carbonic oxide.

J. F. T.

**The Artificial Colouring of Crystals of the Haloid Salts of the Alkali Metals by means of Sodium and Potassium vapour.** BY FRITZ GIESEL. (*Ber.*, 1897, **30**, 156—158).—The similarity between

the colour of blue rock salt and that produced by the action of the cathode rays on crystals of sodium chloride, seemed to suggest the possibility of colouring these crystals by purely chemical means and this is, in fact, readily effected by heating them in a closed tube with sodium or potassium vapour, the colour produced being independent of the metal used.

Under these conditions, potassium bromide and iodide are coloured deep blue; potassium chloride, dark heliotrope, and sodium chloride, yellow to brown, the colour appearing to pervade the whole crystal and not merely to reside on the surface; it is stable in the air, and even in water is retained as long as the crystal remains undissolved, the solution, however, is colourless, and a colourless salt is obtained on evaporating it. At high temperatures, the colour is discharged.

The behaviour of the yellowish-brown sodium chloride is remarkable. On heating, the colour passes gradually from yellow through red to bluish violet, ultimately becoming colourless, but any shade of colour can be retained by cooling at the moment of its production. It is possible, therefore, to obtain a blue shade identical with that of the naturally occurring blue rock salt.

The blue colour of sodium chloride crystals obtained by the action of the cathode rays, and also that of blue rock salt, can be changed into yellow or red under the same conditions, the only difference being that, in the latter, a red fluorescence is always apparent. J. F. T.

**Metallic Precipitation.** By JEAN B. SENDERENS (*Bull. Soc. Chim.*, 1896, [4], 15, 208—221. Compare Abstr., 1896, ii, 106).—The author shows experimentally that when one metal is precipitated from a solution of its nitrate by another metal, the amount of the second metal which goes into solution is more than can be accounted for by the reaction $R''(NO_3)_2 + M'' = M''(NO_3)_2 + R''$.

In the case of copper or cobalt in contact with solutions of silver nitrate, the excess is very slight, and becomes negligable when air is excluded from the apparatus during the experiment. In most cases, however, the metal becomes oxidised at the expense of the nitric acid present, forming a hydroxide or basic nitrate. M. W. T.

**Nickelo-nickelic Hydroxide.** By WILLIAM L. DUDLEY (*J. Amer. Chem. Soc.*, 1896, 18, 901—903).—Nickelo-nickelic hydroxide, $Ni_3O_4,2H_2O$, is obtained by fusing sodium peroxide with metallic nickel in a nickel crucible, at a cherry-red heat. The action is nearly complete at the end of an hour; when cold, the mass is extracted with water, and the crystals which remain are washed several times with boiling water. The last traces of alkali are only removed after some 50 hours' washing with water in a Soxhlet extraction apparatus. Metallic nickel may be removed by means of a magnet. It is uncertain whether the water is derived from sodium hydroxide in the sodium peroxide, or is taken up during the extraction with water. The crystals are lustrous, and almost black, with a slight brownish-bronze hue. They are soft, and dissolve in acids, forming nickelous salts. Water and alkalis have no action. The sp. gr. of the compound is 3·4115 at 32°. When heated to 140°, it begins to lose weight; at 240° the weight remains constant; but at a red heat

further loss is sustained, and nickelous oxide is formed. The compound made in an ordinary nickel crucible usually contains a small amount of cobalt. J. J. S.

**Sulphides of Cobalt and Nickel.** By GABRIEL CHESNEAU (*Compt. rend.*, 1896, **123**, 1068—1071. Compare Abstr., 1895, ii, 228, 247).—When sodium monosulphide is added to a solution of cobaltous chloride, the precipitated sulphide is completely insoluble in an excess of the precipitant. If, however, a solution of the monosulphide saturated with sulphur at the ordinary temperature (containing about 3·7 eq. of sulphur for 1 eq. of sodium) is employed, a black precipitate is obtained, which, although quite insoluble in sodium monosulphide, dissolves in the polysulphide solution to the extent of 6 grams of cobalt per litre at the ordinary temperature. In sodium polysulphide solutions which are not saturated with sulphur, the solubility of the cobalt sulphide very rapidly diminishes. Cobaltous sulphide itself only dissolves in the polysulphide solution to the extent of 0·35 gram of cobalt per litre, the greater solubility of the above-mentioned precipitate being due to the fact that it consists of a persulphide of cobalt probably having the formula $Co_2S_7$. On evaporating the solution of cobalt persulphide in sodium polysulphide in a vacuum, black, crystalline plates separate, which are deliquescent and soluble in water and absolute alcohol, but which were not analysed.

When sodium polysulphide is added to a solution of a nickel salt, a black persulphide is obtained, apparently corresponding with the cobalt compound; this, however, differs from it in being appreciably soluble in the monosulphide and practically insoluble in the polysulphide solution. A. C. C.

**Sulphochromic Acid, a New Acid containing Chromium.** By ALBERT RECOURA (*Bull. Soc. Chim.*, 1896, [3], **15**, 315—321).—Compounds of chromium sulphate with 1, 2, or 3 molecules of sulphuric acid have already been described (Abstr., 1893, ii, 470). By evaporating a solution containing 1 molecule of chromium sulphate to 3, 4, or 5 molecules of sulphuric acid, and heating the product for a day or two at 115°, the following substances separated in crystals—$Cr_2(SO_4)_3$, $4H_2SO_4$, $Cr_2(SO_4)_3$, $5H_2SO_4$, $Cr_2(SO_4)_3$, $6H_2SO_4$. (Compare Abstr., 1893, ii, 528.) On heating the solutions of these substances in water, or leaving them for some days, they deposit a flocculent precipitate of a greenish colour; the addition also of a salt of any metal, even of sodium or potassium, to the original solution, produces a precipitate.

As, from their properties, the three compounds appeared to contain the same central group, the compound $Cr_2(SO_4)_3,4H_2SO_4$ was taken for investigation. On adding a molecular equivalent of cupric chloride to a solution containing a known quantity of this compound, a whitish-green precipitate was formed having the composition $Cr_2O_3,CuO,4SO_3$, but evidently differing from copper chromium sulphate, which is a soluble salt. The compound, when boiled with 8 equivalents of sodium hydroxide, gave sodium sulphate and copper chromite, $Cr_2O_3$, CuO. This may be taken as indicating that, in the compound $Cr_2O_3,CuO,4SO_3$, the copper is directly united to the chromium, and not to the $SO_3$ group. As to the

manner in which the remaining molecules of sulphuric acid, which are left in solution on adding a metallic salt to a solution of $Cr_2(SO_2)_3,4H_2SO_4$ are combined, nothing has been ascertained.

Potassium salts behave in the same manner as copper salts, forming a compound $Cr_2O_3,K_2O,4SO_3$. To these compounds the author has given the name sulphochromites.

*Sulphochromic acid* (compare Abstr., 1896, ii, 27).—When heated to 140—150°, the compound $Cr_2(SO_4)_3,4H_2SO_4$ loses 3 molecules of sulphuric acid, and sulphochromic acid, $(SO_3)_4Cr_2O_2(OH)_2$, is formed; this is a grey, amorphous substance, soluble in water, and giving a precipitate $(SO_3)_4,Cr_2O_3,OM''$ with metallic salts. Its heat of neutralisation is higher than that of sulphuric acid,

$(SO_4)_4Cr_2O_2(OH)_2$ diss. + $Na_2SO_4$ diss. = $(SO_4)_4Cr_2O_2(ONa)_2$ diss. + $H_2SO_4$ diss. ............................................ + 5·1 Cal.,

the presence of the $SO_3$ groups in the compound having a powerful influence on the nature of the hydroxyl groups.

The paper concludes with a note on the isomerism of the sulphochromites and the compounds derived from hydrogen chromium sulphate, and a short note on the preparation of chromites. M. W. T.

**The Silicotungstates.** By GREGOIRE N. WYRUBOFF (*Bull. Soc. franc. min.*, 1896, 19, 219—354).—The fact that valuable information of a purely chemical nature, as opposed to information of a physicochemical character, respecting the valency of the metals can be obtained by a study of the crystallographical properties of their salts, has led the author to make an exhaustive examination of the silicotungstates. In order to determine the valency of a metal, crystallographical evidence of a positive kind must be obtained; it is not legitimate to conclude that a metallic oxide is not a sesquioxide because its sulphate does not form an alum with the alkali sulphates, neither is cadmium to be regarded as not a member of the magnesium group because its sulphate yields none of the hydrates characteristic of the group; and since the author has found that the metals display their distinctive properties most fully in their more complex compounds, he has studied the salts of silicotungstic acid, which have high molecular weights, crystallise well, and are very stable, in order to extend our knowledge of valency.

Silicotungstic acid is best prepared from commercial sodium tungstate by a modification of Marignac's process (*Ann. chim. phys.*, 1864, [4], 3, 5); nitric acid is added to the concentrated aqueous solution of the salt until the precipitate first formed is just dissolved, and after adding excess of gelatinous silica, the liquid is heated, being kept acid by occasionally adding nitric acid, until a test sample is no longer precipitated by hydrochloric or nitric acid; if the heating be too prolonged, silicodecitungstic acid is formed. After filtration, mercurous nitrate, free from mercuric salt, is added, and the precipitate is washed by decantation and decomposed by hot hydrochloric acid; the filtered solution yields pure silicotungstic acid on evaporating to dryness.

Marignac considered silicotungstic acid to be octobasic, having the composition $12WO_3,SiO_2,4H_2O$, because of its behaviour towards carbonates; the author finds, however, that its salts containing $2R_2O$ only

decompose the carbonates of the alkalis, alkaline earths, and magnesium, and also that, until the acid attains the composition $12WO_3,SiO_2,2H_2O$ or $H_4W_{12}SiO_{40}$ (at 370°) it preserves all its properties; the acid must therefore have the latter composition and be tetrabasic. It decomposes nitrates and chlorides, and is only partially decomposed by prolonged boiling with sulphuric acid, it is, however, very readily oxidised by proto-salts; it forms salts with all the uni-, bi-, and tri-valent metals, but not with the tetrad metals. The normal and acid salts usually crystallise well and are extremely soluble in water, alcohol or ether, forming with the last two solvents stable compounds which have not yet been examined.

Silicotungstic acid crystallises below 40° in large, efflorescent tetragonal octahedra [$a : c = 1 : 1{\cdot}0117$] of the composition $H_4W_{12}SiO_{40} + 31H_2O$; this hydrate is analogous in composition to the cubic silicotungstates of the trivalent metals, and morphotropically closely related to them in that it is very nearly cubic and almost isotropic. Above 40°, or from a hydrochloric or nitric acid solution, rhombohedral crystals [$a : c = 1 : 2{\cdot}4719$] of a hydrate containing $24H_2O$ are obtained; they are isomorphous with the silicotungstates of the alkaline earths containing $24H_2O$.

The silicotungstates of the univalent metals are not isomorphous amongst themselves, but differ in degree of hydration and other properties; the solubility both of the normal, acid, and basic salts diminishes rapidly as the atomic weight of the metal increases. The hydrates of the three classes of salts contain less water than the salts of the bi- or tri-valent metals; the silicotungstates of the univalent metals never crystallise with more than $20H_2O$, those of the alkaline earths never crystallise with more than $24H_2O$, those of the magnesium group never combine with more than $27H_2O$, whilst the silicotungstates of the trivalent metals do not crystallise with more than $31H_2O$. It is consequently concluded that, if an oxide RO having a molecular weight greater than 100 forms sparingly soluble silicotungstates containing not more than $20H_2O$, the metal is univalent.

Ammonium forms two colourless, amorphous silicotungstates of the composition $(NH_4)_4W_{12}SiO_{40} + 8H_2O$ and $(NH_4)_4W_{12}SiO_{40},4NH_4{\cdot}OH + 14H_2O$, but yields no acid salt. The minutely crystalline basic sodium salt, dried at 100°, has the composition $Na_4W_{12}SiO_{40},4NaHO + 5H_2O$. The normal salt, $Na_4W_{12}SiO_{40} + 20H_2O$, is dimorphous, crystallising in a stable anorthic form [$a : b : c = 1{\cdot}0320 : 1 : 0{\cdot}9092$. $\alpha = 94°2'$. $\beta = 93°32'$. $\gamma = 88°21$] and in an unstable anorthic form [$a : b : c = 0{\cdot}8056 : 1 : 1{\cdot}1221$. $\alpha = 93°14'$. $\beta = 103°29'$. $\gamma = 88°3'$]; it readily changes into a third anorthic *hydrate* containing $14H_2O$ [$a : b : c = 1{\cdot}6083 : 1 : 0{\cdot}5542$. $\alpha = 90°52'$. $\beta = 95°22'$. $\gamma = 83°34'$], which also crystallises at 35°. Above 40°, or in presence of hydrochloric or nitric acid, an anorthic hydrate of the composition $Na_4W_{12}SiO_{40} + 13H_2O$ crystallises [$a : b : c = 1{\cdot}0932 : 1 : 0{\cdot}9102$. $\alpha = 88°51'$. $\beta = 95°18'$. $\gamma = 86°37'$.] On crystallising the salt from a feebly acid solution at 25—30°, beautiful anorthic plates of the composition $Na_2H_2W_{12}SiO_{40} + 16H_2O$ are deposited [$a : b : c = 1{\cdot}0748 : 1 : 0{\cdot}9521$. $a = 1{\cdot}0748 : 1 : 0{\cdot}9521$. $\alpha = 89°6'$. $\beta = 95°50'$. $\gamma = 85°17'$]. The double salt of the composition $3Na_4W_{12}SiO_{40},4NaNO_3 + 45H_2O$ is also anorthic [$a : b : c = 1{\cdot}0057 : 1 : 0{\cdot}8562$. $\alpha = 89°35$. $\beta = 90°20'$. $\gamma = 91°6'$].

The double potassium salt, $K_4W_{12}SiO_{40},4KHO + 12H_2O$, is soluble in 10 parts of water at 18° and is only indistinctly crystalline. The hexagonal [$a : c = 1 : 0·5500$] hydrate, $K_4W_{12}SiO_{40} + 18H_2O$, loses $12H_2O$ in the air and becomes anhydrous at 105°; the crystals are circularly polarising and are always dextrorotatory, $\alpha_D = 14°4'$. A nitric acid solution at temperatures above 30°, deposits a monosymmetric [$a : b : c = 1·4715 : 1 : 1·9939$. $\beta = 77°6'$] *hydrate*, $K_4W_{12}SiO_{40} + 15H_2O$ and a sulphuric acid solution at 30—34° deposits a monosymmetric [$a : b : c = 1·2148 : 1 : 0·8489$. $\beta = 77°44'$] double salt of the composition $K_4W_{12}SiO_{40},K_2H_2W_{12}SiO_{40} + 29H_2O$.

The *acid rubidium* salt, $Rb_4W_{12}SiO_{40},Rb_2H_2W_{12}SiO_{40} + 22H_2O$ is obtained as an amorphous, white powder, and on treating it with nitric acid and washing with water an amorphous *salt*, $Rb_2H_2W_{12}SiO_{40} + 5H_2O$ is obtained. The *thallium* salt, $Tl_2H_2W_{12}SiO_{40} + 9H_2O$, is also amorphous; the silver salt, $Ag_4W_{12}SiO_{40} + 9H_2O$, is very sparingly soluble and loses $4H_2O$ at 105°. The mercurous salt,

$$Hg_4W_{12}SiO_{40},2Hg_2O + 5H_2O$$

is quite insoluble.

The author considers lithium to be a bivalent metal of atomic weight 14 for the following reasons. Its chloride, nitrate and thiosulphate only are isomorphous with the corresponding sodium salts, and it does not displace the alkali metals from their combinations but readily forms double salts with them; the simple reactions of lithium are also very similar to those of the alkaline earths and very different from those of the alkali metals. Further indication of the bivalency of lithium is found in its affinity for nitrogen, the impossibility of reducing its hydroxide by metals like iron, the sparing solubility of its hydroxide in alcohol and water, the non-existence of a bicarbonate, the instability of its acid sulphate, the ready decomposition of its nitrate by heat, the solubility in alcohol and sparing solubility in nitric acid of its nitrate, the insolubility and decomposition by heat of its carbonate and the insolubility of its fluoride, phosphate, and silicate; the bivalency of lithium is contrary to Dulong and Petit's law and to the periodic law, but to these the author attaches little weight. It is now shown that *lithium silicotungstate*, $Li_2W_{12}SiO_{40}$, is an extremely soluble salt isomorphous with the silicotungstates of barium and calcium; it crystallises in the rhombohedral system [$a : c = 1 : 2·6186$] as a *hydrate* containing $24H_2O$ which is isomorphous with and crystallises in all proportions with the acid. On crystallisation at 40—45° from a nitric acid solution, an anorthic *hydrate* [$a : b : c = 1·1642 : 1 : 0·9681$. $\alpha = 90°$. $\beta = 94°20'$. $\gamma = 86°26'$] containing $14H_2O$ is deposited; it is isomorphous with the hydrate of the sodium salt containing $13H_2O$.

The very soluble acid calcium salt was unsuitable for examination, but the normal salt, $Ca_2W_{12}SiO_{40}$, crystallises at ordinary temperatures in large pseudohexagonal, monosymmetric crystals [$a : c = 1 : 2·6419$] containing $27H_2O$; in presence of nitric or sulphuric acid, a *hydrate* containing $24H_2O$ separates in hexagonal crystals [$a : c = 1 : 2·5045$] whilst at 30°, in presence of nitric acid, an anorthic *hydrate* [$a : b = 0·4228 : 1$. $\alpha = 87° 40'$. $\beta = 90°30'$. $\gamma = 81°6'$] containing $18H_2O$ is deposited. The double *salt*, $Ca_2W_{12}SiO_{40},Ca(NO_3)_2$, crystallises with

$15H_2O$ in monosymmetric prisms [$a:b:c=0·9036:1:1·1820$. $\beta=85°8'$] and with $13H_2O$ in anorthic crystals; it is decomposed by water.

The *strontium* salt, $Sr_2W_{12}SiO_{40}$, crystallises below 30° with $27H_2O$ in rhombohedra [$a:c=1:2·5933$] and at 30°, in presence of nitric acid, in anorthic crystals [$a:b:c=1·0212:1:0·5947$. $\alpha=92°46'$. $\beta=91°16'$. $\gamma=95°18'$] containing $23H_2O$, and also in monosymmetric crystals [$a:b:c=1·3001:1:1·0058$. $\beta=83°14'$] containing $17H_2O$; above 50° a monosymmetric *hydrate* [$a:b:c=1·8452:1:1·5695$. $\beta=75°24'$] containing $16H_2O$ is obtained.

The basic barium salt contains 4 BaO; the normal salt $Ba_2W_{12}SiO_{40}$, crystallises at 30° in hexagonal prisms [$a:c=1:2·6813$] containing $24HO_2$ and above 30° in monosymmetric crystals [$a:b:c=1·7987:1:1·5440$. $\beta=76°7'$] containing $16H_2O$. The *potassium barium* salt, $K_2Ba_2W_{12}SiO_{40}+17H_2O$, crystallises in monosymmetric plates [$a:b:c=0·6471:1:0·6056$. $\beta=81°15'$].

The normal silicotungstates of cerium, lanthanum, and didymium crystallise with $27H_2O$, and are completely isomorphous with the corresponding hydrate of the calcium salt; all are monosymmetric and pseudorhombohedral. It follows that these three rare metals are bivalent and constitute a family very similar to that of the alkaline earths. Thorium silicotungstate also crystallises with $27H_2O$ as a pseudorhombohedral monosymmetric hydrate, and is, therefore, also bivalent; in the following formulæ, the atomic weights Ce = 93, La = 92, Di (Nd and Pr) = 96, and Th = 116 are consequently chosen. Many other arguments, both chemical and crystallographical, are quoted in favour of the bivalency of these metals.

Cerosoceric hydroxide, $Ce_3O_4,3H_2O$, is not soluble in silicotungstic acid, but dissolves on adding nitric acid giving a cerous silicotungstate; *basic cerous silicotungstate*, obtained by the action of a cerous salt on the basic sodium salt, is an insoluble, gelatinous, yellow precipitate. *Cerous silicotungstate*, $Ce_2W_{12}SiO_{40}$, crystallises below 15° with $27H_2O$ in colourless, monosymmetric plates [$a:b:c=1·7090:1:2·6558$. $\beta=89·40'$], whilst at 35° the same hydrate is obtained in rhombohedra [$a:c=1:2·6820$] which become monosymmetric on cooling. The acid *salt*, $Ce_2W_{12}SiO_{40},CeH_2W_{12}SiO_{40}+34H_2O$, crystallises below 35° from a nitric acid solution in yellow, anorthic crystals [$a:b:c=0·3922:1:0·4195$. $\alpha=90°43'$. $\beta=92°20'$. $\gamma=84°38'$].

The normal *lanthanum* salt, $La_2W_{12}SiO_{40}$, crystallises with $27H_2O$ in colourless, efflorescent rhombohedra [$a:c=1:2·6392$]; the monosymmetric form could not be isolated. The acid *salt*,

$$La_2W_{12}SiO_{40},LaH_2W_{12}SiO_{40}+34H_2O,$$

forms greenish, anorthic crystals [$a:b:c=0·4081:1:0·4420$. $\alpha=89°43'$. $\beta=93°8'$ $\gamma=84°29'$].

The normal *didymium* salt, $Di_2W_{12}SiO_{40}$, like the cerium salt, crystallises with $27H_2O$ below 20° in amethyst-red, monosymmetric plates [$a:b:c=1·7000:1:2·6325$. $\beta=89°46'$] and also in an unstable rhombohedral form [$a:c=1:2·6660$]; above 20°, a *hydrate* containing $26H_2O$ is obtained in rhombohedral plates [$a:c=1:1·6636$]. The acid *salt*, $Di_2W_{12}SiO_{40},DiH_2W_{12}SiO_{40}+34H_2O$, is of darker colour [$a:b:c=0·4003:1:0·4262$. $\alpha=89°58'$. $\beta=92°48'$. $\gamma=83°20'$].

The basic *thorium* salt is insoluble, but the normal *salt*, $Th_2W_{12}SiO_{40}$, is very soluble and crystallises with $27H_2O$ like the preceding salts; the rhombohedral form only was measured [$a:c=1:2·6653$]. The acid *salt*, $Th_2W_{12}SiO_{40},2H_4W_{12}SiO_{40}$, crystallises with $45H_2O$ in small, anorthic prisms [$a:b:c=1·0721:1:1·1403$. $\alpha=95°47'$. $\beta=90°6'$. $\gamma=90°16'$].

A mixture of yttria earths from monazite having the molecular weight $RO=88·6$, and consisting mainly of yttria and erbia with a little terbia, was used for preparing the following two salts. The normal *salt*, $(Y,Er)_2W_{12}SiO_{40}+26H_2O$, crystallises in rose-coloured rhombohedra [$a:c:=1:1·7282$] and on crystallising its solution at 30° with nitric acid, anorthic twin crystals [$a:b:c=0·9760:1:0·9967$. $\alpha=92°23'$. $\beta=91°50'$. $\gamma=88°22'$] of the acid *salt*,

$$(Y,Er)_2W_{12}SiO_{40},(Y,Er)H_2W_{12}SiO_{40}+50H_2O,$$

are obtained.

The metals of the magnesium group are characterised by forming normal salts crystallising with $27H_2O$ in the rhombohedral system and by not forming sesqui-acid salts; most of them also yield anorthic hydrates containing $18H_2O$; the axial ratios for both these hydrates are given in the appended table. The rhombohedral salts are very efflorescent, and are obtained at a lower temperature than the anorthic ones.

| R | $R_2W_{12}SiO_{40}+27H_2O$ | $R_2W_{12}SiO_{40}+18H_2O$. | | | |
|---|---|---|---|---|---|
| | $a:c$ | $a:b:c$ | $\alpha$ | $\beta$ | $\gamma$ |
| Mg | 1:2·6600 | 0·4068:1:0·4021 | 86° 50′ | 90° 35′ | 90° 11′ |
| Mn | 1:2·6549 | 0·4018:1:0·4088 | 87 0 | 90 11 | 91 0 |
| Co | 1:2·6760 | 0·4067:1:0·4055 | 87 9 | 91 8 | 89 23 |
| Ni | 1:2·6392 | 0·4054:1:0·4166 | 86 48 | 91 6 | 89 32 |
| Cu | 1:2·6706 | — | — | — | — |
| Zn | 1:2·6279 | 0·4034:1:0·3911 | 86 6 | 91 26 | 91 5 |
| Cd | 1:2·6123 | — | — | — | — |

A very efflorescent cupric salt containing $29H_2O$ is obtained below 10°; from 10—40°, the $27H_2O$ hydrate is obtained, and above 40° the hydrate with $18H_2O$. In like manner, the zinc salt crystallises with $29H_2O$ at 10°, with $27H_2O$ at 10—25°, and with $18H_2O$ above 25°. The *cadmium* salt is obtained as an anorthic hydrate [$a:b:c=0·3784:1:0·3207$. $\alpha=88°7'$ $\beta=96°9'$. $\gamma=89°31'$] containing $23H_2O$ by evaporating its nitric acid solution at 30°; a *salt* of the composition

$$2Cd_2W_{12}SiO_{40},H_4W_{12}SiO_{40}+42H_2O$$

was also prepared.

The *mercuric* salt, $Hg_2W_{12}SiO_{40}$, is extremely soluble and crystallises at 25° in anorthic prisms [$a:b:c=0·9848:1:1·0191$. $\alpha=97°40'$. $\beta=94°22'$. $\gamma=90°40'$] containing $15H_2O$; its solution decomposes on boiling, giving an insoluble basic salt and silicotungstic acid. The *lead* salt, $Pb_2W_{12}SiO_{40}+21H_2O$, is obtained under certain conditions

and forms monosymmetric crystals. [$a : b : c = 1·7963 : 1 : 1·1203$. $\beta = 81°35'$]. The basic *salt*, $Pb_2W_{12}SiO_{40},2PbO + 20H_2O$, is a sparingly soluble, amorphous powder.

The normal silicotungstates of the trivalent metals give a cubic hydrate with $31H_2O$ at ordinary temperatures, and at 30—35° a hydrate containing $29H_2O$ isomorphous with the $27H_2O$ hydrates of the magnesium series; at higher temperatures, a monosymmetric hydrate with $20H_2O$ is usually obtained. The trivalent metals do not form sesqui-acid tungstates, but they give extremely soluble, uncrystallisable basic salts. On adding ammonia to the solution, a precipitate is obtained soluble in excess of the reagent. The author shows that beryllium possesses the properties characteristic of the trivalent metals, and therefore concludes that, in spite of the chemical evidence, beryllia has the composition $Be_2O_3$.

*Beryllium silicotungstate*, $Be_4(W_{12}SiO_{40})_3$, crystallises below 45° as a cubic hydrate containing $93H_2O$, and above 45° as a rhombohedral hydrate [$a : c = 1 : 2·4282$] containing $87H_2O$; in presence of nitric acid at 30°, a hydrate containing $45H_2O$ is obtained. Aluminium yields a cubic *hydrate* with $93H_2O$, and a rhombohedral *hydrate* [$a : c = 1 : 2·6655$] with $87H_2O$, whilst the nitric acid solution deposits a monosymmetric *hydrate* [$a : b : c = 0·8521 : 1 : 1·0894$. $\beta = 73°20'$] containing $60H_2O$ at 35°. *Chromium silicotungstate*, $Cr_4(W_{12}SiO_{40})_3$, gives the $93H_2O$ hydrate below 25° and the rhombohedral hydrate [$a : c = 1 : 2·5354$] with $87H_2O$ above 25°, whilst the monosymmetric hydrate [$a : b : c = 0·8658 : 1 : 1·0798$. $\beta = 73°44'$] with $6H_2O$ is deposited by the nitric acid solution at 30°. *Ferric silicotungstate* yields the cubic hydrate with $93H_2O$ and the monosymmetric hydrate [$a : b : c = 0·8465 : 1 : 1·0897$. $\beta = 73°20'$] with $60H_2O$, but the hydrate with $87H_2O$ could only be obtained as an isomorphous mixture with the corresponding aluminium salt. *Gallium silicotungstate*, $Ga_4(W_{12}SiO_{40})_3$, gives the cubic hydrate with $93H_2O$, the rhombohedral salt [$a : c : = 1 : 2·6346$] with $87H_2O$, and the monosymmetric hydrate [$a : b : c = 0·9057 : 1 : 1·1585$. $\beta = 74°20'$] with $60H_2O$.

The behaviour of the uranium silicotungstates makes it probable that uranic oxide has the composition $U_2O_3$ and that the metal has an atomic weight of 120. On heating silicotungstic acid solution with different quantities of uranic nitrate, evaporating off the nitric acid, and crystallising, a series of crystalline cubic salts of the following compositions ($U = 120$) was obtained.

$$U_4(W_{12}SiO_{40})_3 + 87H_2O,2U_2H_6(W_{12}SiO_{40})_3 + 174H_2O.$$
$$U_4(W_{12}SiO_{40})_3 + 87H_2O,U_2H_6(W_{12}SiO_{40})_3 + 87H_2O.$$
$$2U_4(W_{12}SiO_{40})_3 + 174H_2O,U_2H_6(W_{12}SiO_{40})_3 + 87H_2O.$$
$$U_4(W_{12}SiO_{40})_3 + 87H_2O.$$
$$U_4(W_{12}SiO_{40})_3 + 87H_2O,U_2O_3,H_2O + 87H_2O.$$
$$U_4(W_{12}SiO_{40})_3 + 87H_2O,3U_2O_3,3H_2O + 261H_2O.$$
$$U_4(W_{12}SiO_{40})_3 + 87H_2O,4U_2O_3,4H_2O + 348H_2O.$$

W. J. P.

**Antimonic Tungstates.** By L. A. Hallopeau (*Compt. rend.*, 1896, **123**, 1065—1068).—When an excess of antimonic acid is boiled for several hours with a solution of potassium paratungstate, it dissolves,

and, on filtering, crystals of potassium antimoniotungstate are deposited having the composition $2WO_3,3KSbO_3 + 8H_2O$, and differing from the antimoniotungstate described by Gibbs. This compound forms small botryoidal masses, composed of a very large number of prismatic, twinned crystals, which are highly refractive and act powerfully on polarised light. They are permanent in the air, lose $6H_2O$ at 100°, and, on ignition, yield potassium tungstate, tungstic acid, and antimonic acid. When fused with an excess of sodium carbonate, carbonic anhydride is evolved and sodium tungstate, potassium tungstate and trisodium antimonate are formed. On treating the fused mass with water, a crystalline sodium antimonate, $Sb_2O_5,Na_2O + 6H_2O$, is left. Potassium antimoniotungstate is decomposed by hydrochloric, sulphuric, and nitric acids with formation of tungstic acid, and by hydrogen sulphide with precipitation of antimony and tungsten. When well-washed silver antimoniotungstate is treated with the theoretical quantity of hydrochloric acid, and the solution evaporated in a vacuum, a transparent, vitreous, residue of *antimoniotungstic acid*, $4WO_3,3Sb_2O_5,3H_2O + 8H_2O$, remains, which does not lose weight at 100°. A. C. C.

---

## Mineralogical Chemistry.

---

**Heavy Liquids for the Separation of Minerals.** By JAN W. RETGERS (*Jahrb. f. Min.*, 1896, ii, 183—195. Compare this vol., ii, 45). —The author gives the results of experiments made with the object of finding amongst the nitrates and double nitrates of the heavy metals (silver, mercury, lead and thallium) a heavy liquid suitable for the separation of minerals, especially sulphides. In many cases, these are unsuitable, owing, usually, to their easy decomposition. Those found to be the more suitable are the following.

Mercurous nitrate, $HgNO_3 + H_2O$, melts at 70° to a clear, mobile liquid of sp. gr. 4·3; it is miscible with water, and is much less expensive than the other salts; basic nitrates, however, separate on heating.

Thallium nitrate (m. p. 205°, sp. gr. 5·3) does not mix with water, and, like the thallium silver nitrate (m. p. 70°, sp. gr. 4·8), it acts on sulphides. Thallium mercuric nitrate (m. p. 110°, sp. gr. 5·0) does not act on sulphides, but the liquid is cloudy.

Thallium mercurous nitrate (m. p. 76°, sp. gr. 5·3) gives a clear, mobile liquid, which is miscible with water and does not act on sulphides; this is the most convenient liquid described, and ought to be very useful in the separation of mineral sulphides, which so often enclose impurities. L. J. S.

**Occurrence of Rubies in Burma.** By MAX BAUER (*Jahrb. f. Min.*, 1896, ii, 197—238).—Material from the Sagyin (Sadschijin)

Hills, which are about 20 miles north of Mandalay, is described. Here ruby occurs in a white, crystalline marble with spinel, chondrodite apatite, phlogopite, hornblende, pyrites, pyrrhotite and graphite. The marble is usually dolomitic, although at times magnesium is absent; the mean of two analyses is

| $CO_2$. | CaO. | MgO. | Insol. | Total. | $CaCO_3$. |
|---|---|---|---|---|---|
| 44·5 | 48·65 | 6·4 | 0·2 | 99·75 | $86\frac{2}{3}$ |

The well-developed crystals of ruby have rounded edges and show etch figures, but are not surrounded by alteration products: a detailed crystallographic description is given; lamellar twinning on $c$(111) and $r$(100) is rare; $e${110} is given as a new form. The chondrodite occurs plentifully as irregular grains; analysis of fresh material of a greenish yellow colour gave

| $SiO_2$. | MgO. | FeO. | $Al_2O_3$. | CaO. | F. | $H_2O$. | Total. | Sp. gr. |
|---|---|---|---|---|---|---|---|---|
| 37·41 | 47·90 | 7·40 | 2·60 | 0·90 | 1·15 | 1·23 | 98·59 | 3·197 |

The sp. gr. of dull, weathered material is 3·175, and of white material still more weathered 3·138.

According to the observations of Noetling, the limestone is of organic origin, and is of wide distribution in Burma; it has become crystalline, and the various minerals have been developed in it, by the action of contact metamorphism. This mode of origin of the limestone and rubies is quite different from that put forward by Brown and Judd (Abstr., 1896, ii, 32) in their description of the adjoining Mogok district.

In a general review of the modes of occurrence of ruby and sapphire, it is pointed out that these two varieties of corundum do not, as a rule, occur together: ruby usually occurs in crystalline limestone with spinel, whilst sapphire is more characteristic of granites and crystalline schists and is not associated with spinel. The sapphires found in volcanic rocks are probably foreign enclosures derived from granites, &c.

L. J. S.

**Chemical Nature of Vesuvian [Idocrase].** By CARL F. RAMMELSBERG (*Jahrb. f. Min.*, 1896, ii, 157—164).—Reducing the bases to the equivalent R′, the mean ratios deduced from 41 published analyses are R′ : Si = 4·44 : 1 and R‴ : R″ = 2 : 1, individual analyses showing, as a rule, only small variations from these means; the ratio R′ : R″, however, varies from 1 : 1·9 to 1 : 11·0. Assuming R′ : Si = 4·5 : 1, the formula for idocrase becomes $R'_{18}Si_4O_{17} = 3R'_4SiO_4, R'_6SiO_5$, or in detail $R'_{18}Si_4O_{17}$, $n(4R''_9Si_4O_{17}, 3R'''_6Si_4O_{17})$, where $n$ is 1, 1·5, 2, or 4. In the calculations, the titanium is taken with the silica; R′ = H, K, Na; R″ = Ca, Mg, Fe, Mn; R‴ = Al, B, Fe, Mn; and fluorine has been neglected, being considered to form a fluosilicate of the same composition as the oxysilicate. Various anomalous analyses are discussed in detail, and are brought into agreement with the above formula. If the titanium be calculated as $Ti_2O_3$, some FeO must be omitted, as $Ti_2O_3 + Fe_2O_3 = 2TiO_2 + 2FeO$: the amount of FeO found in the analysis gives a basis for calculating the relative amounts of $TiO_2$ and $Ti_2O_3$.

L. J. S.

**Theory of Plagioclase mixing.** By CARL F. RAMMELSBERG (*Jahrb. f. Min.*, 1896, ii, 165—181).—If Tschermak's theory, that the plagio-

clastic felspars are isomorphous mixtures of albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$), be true, then for every ratio of Na : Ca there must be a certain fixed ratio of Al : Si. This was pointed out by the author in 1872, and in the present paper he gives the ratios, calculated from numerous published analyses, of labradorite, andesine, and oligoclase, and finds that for 80 per cent. there is an agreement with theory. The cases of disagreement are to be explained by imperfect analyses and impure material; these usually show an excess of sodium over that calculated from the ratio Al : Si. These exceptions also do not agree with the theory of Sartorius von Waltershausen, that the plagioclases are mixtures of $mNa_2Al_2Si_6O_{16} + nCaAl_2Si_6O_{16}$ with $mCaAl_2Si_2O_8 + nNa_2Al_2Si_2O_8$. The simplest and most frequent mixtures are: labradorite, $Ab_1An_3$, $Ab_1An_2$; andesine, $Ab_3An_4$, $Ab_1An_1$, $Ab_5An_4$; oligoclase, $Ab_3An_2$, $Ab_2An_1$, $Ab_3An_1$. L. J. S.

**Relation between Dynamometamorphism and Molecular Volume.** By FRIEDRICH BECKE (*Jahrb. f. Min.*, 1896, ii, 182—183).—Comparing certain massive rocks with their dynamometamorphic representatives, it is seen that the two contain different minerals composed of the same elements; for example, porphyries with orthoclase are altered to sericite-schists. Another change can be expressed as follows

$$\underset{\text{Plagioclase.}}{x(NaAlSi_3O_8) + 4(CaAl_2Si_2O_8)} + \underset{\text{Orthoclase.}}{KAlSi_3O_8} + 2H_2O$$

$$= \underset{\text{Albite.}}{x(NaAlSi_3O_8)} + \underset{\text{Zoisite.}}{2(HCa_2Al_3Si_3O_{13})} + \underset{\text{Muscovite.}}{H_2KAl_3Si_3O_{12}} + \underset{\text{Quartz.}}{2SiO_2}.$$

Neglecting the albite molecules, the sum of the molecular volumes on the left hand side of this equation is 547·1, and on the right hand side 462·5. In the altered rock, therefore, the elements form minerals occupying the least possible space. This explains the frequent occurrence of garnet, mica, epidote, and other minerals of high specific gravity in the crystalline schists. The case of hornblende taking the place of augite and olivine seems to be an exception, but later analyses show the presence of water in this hornblende, which may then have a lower molecular volume than the corresponding augite + water.

L. J. S.

**Analysis of Water from a new Iodine Spring.** By ANDREAS LIPP (*Ber.*, 1897, **30**, 309—312).—The water of the Marien spring, situated in the parish of Seeg in Bavaria, is colourless, and has a temperature of from 7—8° at all seasons, and a sp. gr. of 1·00216 at 17°. It has a feebly alkaline reaction, and becomes slightly brown in contact with the air, owing to the separation of small quantities of free iodine. Its composition is as follows, in grams per litre—I, 0·01487; Br, 0·01178; Cl, 1·45660; $SiO_2$, 0·0065; Na, 0·914; CaO, 0·1605; MgO, 0·0615; $Fe_2O_3$, 0·00250; $CO_2$, combined 0·15694, free or half combined, 0·185. J. F. T.

# Physiological Chemistry.

**Influence of Atmospheric Oxygen on Metabolism.** By PAUL VON TERRAY (*Pflüger's Archiv*, 1896, 65, 393—446).—The total metabolic changes in dogs and rabbits are independent, within wide limits, of the composition of the inspired air; even when the oxygen was only present to the extent of 10·5 per cent., although the respirations become deeper, the nitrogen and carbonic anhydride secretion showed practically no change. The only difference at the higher limit (87 per cent. of oxygen) was an increase in the excretion of carbonic anhydride.

Below 10·5 per cent. of oxygen, the compensatory power of the body is lost, and the lack of oxygen is felt; the amount of carbonic anhydride is greatly, and of nitrogen slightly, increased. The rise in the output of carbonic anhydride cannot be explained by increase of muscular work, but is due to the entrance into the blood of organic acids; the urine contains lactic and oxalic acids, and sometimes albumin.

W. D. H.

**Influence on Metabolism of dividing the Nutriment into several Meals.** By FRANZ VON GEBHARDT (*Pflüger's Archiv*, 1896, 65, 611—626).—In as pure proteid nutrition as possible, the animal becomes thinner; this is due to loss of fat, and of water. Nitrogen-apposition can be considerable, even when the loss of body weight occurs.

By dividing the nutriment into several meals daily, the organism retains more nitrogen than if all the food for the day is given in one dose. This occurs even when the digestive and absorptive powers of the alimentary tract are not unduly taxed by the single large meal. It is, therefore, advisable to divide the nutriment into several meals.

W. D. H.

**Changes of the Fat of Chyle in the Blood.** By WILHELM COHNSTEIN and HUGO MICHAELIS (*Pflüger's Archiv*, 1896, 65, 473—491).—The blood has the property of causing the disappearance of the fat of the chyle, introduced either in the natural way or by artificial injection. This depends on the presence of oxygen, and is associated with the corpuscles of the blood. The red corpuscles contain a substance which has this *lipolytic* function; the fat is changed into a substance insoluble in ether; this substance is not gaseous, but solid; water and carbonic anhydride were not found in experiments *in vitro*. The change the fat undergoes is probably saponification; but further work is in hand on the question.

W. D. H.

**Course of Excretion of Nitrogen in Man.** By RUDOLF ROSEMANN (*Pflüger's Archiv*, 1896, 65, 343—392).—The nitrogen in the urine was estimated by Kjeldahl's method in successive portions during the course of the day, the maximum occurring between 9 and 11 a.m., the minimum from 1 to 3 p.m. The influence of meals, hunger,

exercise, and other factors was also investigated, and the results are given in numerous tables. W. D. H.

**Occurrence and Detection of Nucleohiston in Urine.** By ADOLF JOLLES (*Ber.*, 1897, **30**, 172—174).—A sample of urine in a case of *pseudoleucœmia* was found to yield a voluminous precipitate with acetic acid, the relatively strong phosphorous reaction of this on the one hand, and the absence of a precipitate on saturation with magnesium sulphate on the other, seemed to indicate the presence of nucleohiston; this was isolated, and purified by dissolving it in sodium hydroxide and reprecipitating with acetic acid, the process being repeated twice. From 600 c.c. of urine, 0·1936 gram of the compound was obtained in this way, 3·14 per cent. of phosphorus being found in it by the ammonium molybdate method. A second experiment, using a larger quantity of urine, yielded a substance containing 3·25 per cent. of phosphorus; these results agree with the 3·025 per cent. observed by Lilienfeld in nucleohiston.

On treating the precipitate with dilute hydrochloric acid for some hours, and filtering, a solution was obtained which, on the one hand, gave a flocculent precipitate with ammonia, a reaction characteristic of histon, and, on the other, the biuret reaction with sodium hydroxide and copper sulphate. Finally, the coagulability of the proteid was determined, the resulting coagulum being soluble in mineral acids.

It is therefore highly probable that the precipitate produced by acetic acid in this sample of urine is identical with nucleohiston.

J. F. T.

## Chemistry of Vegetable Physiology and Agriculture.

**The Changes which take place in Milk, either spontaneously or during Culinary Processes.** By ANTOINE BÉCHAMP (*Bull. Soc. Chim.*, 1896, [4], **18**, 248—272. See this vol., ii, 113).—A continuation of a historical review of the subject. M. W. T.

**Detection and Distribution of Glucase, the Enzyme of Maltose.** By MARTINUS W. BEYERINCK (*Bied. Centr.*, 1896, **25**, 753—757; from *Centr. Bakt. Par.*, **1**, 2 Abt., 221, 265, and 329).—In this paper, the term amylase has been adopted for all the starch-decomposing enzymes, whilst those which simultaneously produce maltose and achroodextrin from starch are termed granulases.

The following methods, employed for the detection of these substances, depend on their power of diffusion. To detect the two amylases in barley, for instance, thin sections are placed on the surface of a solidified mixture of 10 per cent. gelatin solution with about 0·5 per cent. of potato starch; the maltase and granulase diffuse into the gelatin, producing, by amylolytic action, a visible circular field of diffusion. To determine the nature of the enzymes, the gelatin plate is treated with potassium iodide, when the diffusion field shows an inner, colourless zone, and an outer, reddish-violet zone, the rest of the gelatin

being blue. Maltose diffuses more quickly than granulase, and as the former produces (besides maltose) erythrodextrin, and the latter achroodextrin, the appearance of the gelatin plate as described is explained.

Another method is given which depends on the fact that microbes are very selective as regards certain nutritive substances, especially sugars. By means of a suitable substratum used in plate cultivations, the production of a particular sugar in consequence of amylolytic action is at once indicated by the growth of previously inoculated microbes. *Sacch. spiculatus* was found to be suitable, since it assimilates glucose but not maltose and dextrin.

According to Wysman, malt amylase consists of maltase and dextrinase. The latter is now shown to be a product of the action of heat on malt amylase. It is proposed to name the second enzyme, which occurs naturally in barley, granulase. The progressive destruction of the starch molecule is shown in the following table, in which the signs + and – indicate respectively that the substance in question is produced, or not produced, by the action of the amylase.

| | From starch granulose | | | | From erythrodextrin | | | From maltodextrin | | From Maltose |
|---|---|---|---|---|---|---|---|---|---|---|
| | Erythrodextrin | Maltodextrin | Maltose | Glucose | Maltodextrin | Maltose | Glucose | Maltose | Glucose. | |
| 1. Glucase | – | +* | +* | + | +* | + | + | +* | + | + |
| 2. Maltase | +* | – | + | – | – | + | – | + | – | – |
| 3. Granulase | – | +* | + | – | +* | + | – | + | – | – |

Only the products formed in the breaking up of starch granulose are included in the table, as the other substances formed are not suitable for characterising the amylases.

Glucase does not seem to be widely distributed in plants and animals; sorghum contains a good deal, rice less, barley, wheat and rye only traces. It was not found in ordinary grass, but could readily be detected in maize leaves. Most seeds with mealy endosperm, belonging to the dicotyledons, contain maltase and glycase, whilst granulase is only produced during germination. As regards animal juices and organs, the liver alone was found to contain much glycase. It seems, however, to be widely distributed among the mould fungi.

N. H. J. M.

**Enzyme Action.** By G. Harris Morris (*J. Fed. Inst. Brewing*, 1896, **2**, 350—361).—A brief historical account of the various enzymes at present known and their mode of action is given, after which the author describes in detail his experiments on the hydrolytic action of yeast on maltose (Proc., 1895, 46). The recently published results of Fischer (Abstr., 1895, 441) are confirmed, and the following additional observations are recorded. No conversion of maltose into dextrose occurred in the presence of an alcoholic solution of thymol, 25 per cent. alcohol, or a half-saturated aqueous solution of ether. The hydrolysis of maltose by moist yeast is now known, therefore, to take place in the presence of toluene, thymol, or a saturated aqueous solution of ether, but not in the presence of the first-mentioned series of substances or of chloroform, or when the digestion is effected in the absence of any antiseptic. It is ex-

* Intermediate products which undergo further change.

tremely probable that the fermentation of maltose is accompanied by its hydrolysis, the two changes taking place practically simultaneously. The author fails to find any evidence of the existence of a maltose-hydrolysing enzyme in malt. A. C. C.

**Transpiration of the Potato.** By POLJANEC (*Bied. Centr.*, 1896, **25**, 786; from *Oesterr. bot. Zeit.*, 1895).—The daily transpiration of unpeeled potatoes as compared with tubers which had been half-peeled (that is, freed from dead periderm), and with tubers which had been completely peeled, was found to be as 1 : 4 : 200. The results show the great power of the periderm in checking transpiration, and also that the suberised cells, especially of newer organs, allow the passage of water vapour. The numbers given do not apply generally, as transpiration is influenced by variety. N. H. J. M.

**Fruit of Myroxolon Pereiræ and of White Peru Balsam.** By H. GERMANN (*Arch. Pharm.*, 1896, **234**, 641—647).—The seeds of *Myroxolon Pereiræ* often exhibit on their surface well-developed crystals of coumarin, which apparently does not occur in the interior of the seed. The fats which are present consist of palmitin, stearin, and olein. The finely powdered shells of the seeds were extracted first with hot alcohol, and then with ether; the hot alcoholic solution, on cooling, yielded *myroxocercin*, $C_{12}H_{20}O$, a reddish powder of indifferent nature. The alcoholic solution, on distillation, left a residue from which boiling water extracted a tannin and glucose. Part of the residue insoluble in water dissolved in 1 per cent. potash, but was precipitated again on the addition of concentrated potash. After several recrystallisations from alcohol, a pure compound *myroxofluorin*, $C_{42}H_{64}O_{10}$, was obtained.

*Myroxol*, $C_{46}H_{68}O_{10}$, a substance of alcoholic nature, and *myroxoresen*, $(C_7H_{10}O)_n$, were also isolated; the latter is not decomposed by fusion with potash, and after prolonged treatment with concentrated nitric acid yields picric acid.

The ethereal extract yielded a substance *myroxin*, $C_{23}H_{36}O$.

The author has also investigated two specimens of balsam from the fruits of Peru balsam trees. J. J. S.

**The Tannin of Hops.** By JOHN HERON (*J. Fed. Inst. Brewing*, 1896, **2**, 162—180).—The author considers Löwenthal's method by far the most accurate for the estimation of tannin in hops. Experiments are recorded showing the disappearance of tannin which occurs during the storage of hops. One sample, which in 1883 contained 6·2 per cent. of tannin, in 1891 contained only 1·3 per cent. In some cases, after the lapse of four years the tannin had entirely disappeared.

It is probable that phlobaphen (the condensation product of hop tannin described by Etti) is first formed, and that this undergoes oxidation to some substance allied to gallic acid, and that finally compounds are formed which are not acted on by the potassium permanganate solution employed in the determination. The greater part of the change takes place during the first year of storage. Hops which have been sulphured on the poles do not deteriorate so rapidly in this respect as those which have not been so treated. The author finds that, contrary to general opinion, the hop tannin does not cause the precipitation of proteid sub-

stances from the wort during the boiling in the copper, but is of opinion that combination between certain nitrogenous constituents of the wort and the tannin occurs, resulting in the formation of a soluble substance, *tanno-peptone*, which is readily soluble in solutions of organic acids, and which resembles peptone in its general properties. Samples of hops rich in tannin were also found to be rich in those resins and bitter substances which are of value to the brewer. A. C. C.

**Occurrence of Cytisine in different Papilionaceæ.** By PIETER C. PLUGGE and A. RAUWERDA (*Arch. Pharm.*, 1896, **234**, 685—697. Compare Abstr., 1896, ii, 61.)—The authors have examined the seeds of the plants previously enumerated, together with a number of others, for cytisine. The alkaloid was tested for by the method recommended by Van de Moer, by means of ferric chloride (5 per cent. solution) and hydrogen peroxide (0·05 per cent. solution). Cytisine has been found in the following 23 species belonging to this order, in addition to those already mentioned (*loc. cit.*). *Cytisus Attleanus*, *C. candicans* (Lam.), *C. formosissimus*, *C. monspessulanus* (L.), *C. ponticus*, *C. ruthenicus* (Fisch.), *C. scoparius* (Link.), *Ulex hibernicus* (G. Don.), *U. Jussiæi* (Webb), *U. parviflorus* (Pourr.), *Genista ephedroïdes* (D. C.), *G. florida*, *G. monosperma*, *Sophora flavescens*, *S. sericea*, *S. angustifolia*, *Baptisia alba*, *B. bracteata*, *B. exalata*, *B. leucantha*, *B. minor*, *B. perfoliata*, and *B. versicolor*.

Cytisin, however, could not be identified in *Cytisus æolicus* (Guss.), *C. canescens*, *C. Everestianus* (Carr), *C. falcatus* (Waldst and Kit.), *C. pullulans* (Kit.), *C. purpureus* (Scop.), *C. racemosus* (Hort), *C. ramosissimus*, *C. Rochelii* (Wiersb.), *C. serotinus* (Kit.), *C. sessiliflorus* (Poir.), *C. triflorus* (l'Herit.), *Genista Andreana*, *G. canariensis*, *Sophora alata*, *S. alopecuroïdes*, *Baptisia leucophæa*, *Coronilla Emerus*, *C. glauca*, *Robinia pseudacacia* (L.), *Wistaria sinensis* (Nutt.), *Albizzia stipulata*, *Amorpha fructicosa* (L.), *Anthyllis tetraphylla* (L.), *Arthrolobium scorpoïdes*, *Caragana arborescens*, *Desmodium canescens* (D. C.), *Gleditschia sinensis*, *G. triacanthos*, *Kennedya rubicunda*, *Psoralia capitata*, and *Tetragonolobus purpureus*. J. J. S.

**Phosphoric Acid in Barley and Malt.** By AUG. FERNBACH (*J. Fed. Inst. Brewing*, 1896, **2**, 128—140).—The author has made estimations of the percentages of soluble and insoluble phosphoric acid in a number of samples of barley, and in the malts prepared from them, with the object of ascertaining the nature of the changes taking place in the phosphates of the grain during the malting process. He finds that, in eight samples out of nine, a considerable proportion of the insoluble phosphates is rendered soluble, and that the percentages of soluble phosphoric acid (calculated on the total phosphoric acid) are much more uniform in the malts than in the barleys. At the same time, the percentage of total phosphoric acid is reduced. In the ninth sample experimented with, there was a diminution of the soluble phosphates, due to the fact that the original barley contained almost the whole of its phosphoric acid in the soluble state, and that a very hard water was employed for steeping, the phosphoric acid being therefore precipitated, as insoluble phosphates. It is suggested that organic acids produced during germination react with the insoluble dibasic and tribasic phosphates, converting them into soluble acid phosphates. Malt infusions always require the addition of small quantities of acid in order to render them neutral

to methyl-orange, and of small quantities of alkali to render them neutral to phenolphthalein, from which it is inferred that such infusions contain no free acids, but only acid salts, chiefly phosphates. A table is given showing the results of such titrations in the case of twelve samples of malt. Free acid is found to exercise a distinctly retarding effect on the saccharification of starch by diastase, whilst the acid phosphates exert no such unfavourable action. A. C. C.

[NOTE BY ABSTRACTOR.]—Brown and Morris have found that small quantities of lactic and other free acids distinctly favour the action of diastase on starch.

**Swedish Fodder Plants.** By A. G. KELLGREN and LARS F. NILSON (*Bied. Centr.*, 1896, **25**, 732—736; from *Kgl. landtbruks-akad.*, No. 31 1895, 1—93; comp. *Bied. Centr.*, 1894, **23**, 249, and Abstr., 1893, ii, 592).—The plants examined were all collected near the river Lule at the arctic circle. The vegetation was strongest close to the river, where *Carex acuta*, and especially *C. aquatilis*, which grew to the height of about 5 feet, were found. At some distance from the river, the predominant vegetation consisted of *C. ampullacea Goodeenovii* and *vesicaria*, besides some varieties of *Eriophorum* and *Juncus*, whilst the marshy land beyond is covered with herbage, including those varieties already mentioned and a number of others besides.

The following average results are given (per cent. of dry substance). 1. *Gramineæ*. 2. *Cyperaceæ*. 3. *Juncaceæ*. 4. Miscellaneous herbage. 5. Trees and bushes (*Arctostaphylus alpina*, *Betula odonta*, *Salix herbacea*). 6. *Equisetaceæ*. 7. Lichens (*Alectoria jubata*).

| | Total nitrogen. | Ether extract. | Cellulose. | N free extract. | Digestibility co-efficient of nitrogen. | Amide nitrogen. | Ash. |
|---|---|---|---|---|---|---|---|
| 1. | 1·54 | 1·86 | 34·02 | 48·67 | 77·0 | 0·27 | 5·85 |
| 2. | 2·27 | 2·28 | 26·68 | 50·59 | 59·8 | 0·39 | 6·27 |
| 3. | 1·72 | 1·99 | 26·25 | 55·73 | 57·5 | 0·27 | 5·29 |
| 4. | 2·41 | 2·47 | 22·37 | 50·84 | 76·7 | 0·32 | 9·25 |
| 5. | 2·70 | 4·41 | 12·10 | 62·62 | 56·9 | 0·17 | 3·97 |
| 6. | 2·67 | 2·29 | 17·17 | 47·77 | 82·6 | 0·53 | 16·10 |
| 7. | 0·75 | 0·99 | 1·17 | 91·54 | 29·4 | 0·13 | 1·49 |

The much greater food value found for the *Cyperaceæ* (2) as compared with the *Gramineæ* (1), is in accordance with the preference shown by the inhabitants for the former. With regard to trees and bushes (5), large quantities of leaves (especially birch leaves) are used in many parts of the country, and the plants examined probably form an essential portion of the winter food of reindeer. *Equisetum fluviatile*, as green fodder, is said to be favourable to milk production; it is also made into hay. *E. palustre* and *E. arvense* are used for feeding horses and cows respectively. N. H. J. M.

**Analyses of Norwegian Hay.** By FR. WERENSKIOLD (*Bied. Centr.*, 1896, **25**, 736—737; from *Tidsskr. Norsk. Landbr.*, 1896, **3**, 328—332. Compare Abstr., 1895, ii, 324).—The results of new experiments show that the composition and digestibility of different samples of the same plant vary considerably. There seems, however, to be a distinct

difference between *Leguminosæ* and grasses. The following percentage results were obtained with different kinds of hay.

| | Crude proteids. | Digestible proteids. | Indigestible proteids. | Amides. | Coefficient of digestibility of crude proteids. | Coefficient of digestibility of proteids. |
|---|---|---|---|---|---|---|
| *Trifolium pratense* | 11·38 | 2·28 | 5·04 | 4·06 | 55·7 | 31·1 |
| „ *hybridum* | 11·38 | 2·55 | 4·21 | 4·62 | 63·0 | 36·2 |
| *Anthyllis vulneraria* | 11·52 | 4·03 | 3·15 | 4·34 | 72·7 | 56·2 |
| 19 Grasses Max. | 6·10 | 2·75 | 2·69 | 2·57 | 79·4 | — |
| 19 Grasses Min. | 3·08 | 0·87 | 0·44 | 0·62 | 55·9 | — |

A sample of *Astragalus Oroboides* (collected 13th July) furnished hay containing 24·38 per cent. of crude proteids; the digestibility coefficient was 86·5. The percentage of indigestible proteids was 3·30, digestible proteids 10·04, and amides 11·04. N. H. J. M.

**Examination of Linseed Meal.** By FRITZ W. A. WOLL (*Ann. Rep. Agr. Exp. Stat. Wisconsin* for 1895, **12**, 64—85).—Linseed cake prepared by the old method, in which the moistened seeds were heated to about 70—80° and pressed, contained 6—7 per cent. of fat. In the new method, the crushed and heated seeds are extracted about 12 times with light petroleum, and the seeds, after being steamed to remove the light petroleum, are dried and ground. The meal so obtained contains fat (3·2 per cent.) and proteids (37·9 per cent.), whilst by the old method it contained 7·2 and 35·9 per cent. of fat and proteids respectively. The proteids are abnormally high owing to the climatic conditions of 1894. The lower digestibility of the residues extracted with light petroleum is attributed to the steaming.

The two kinds of meal can be distinguished by means of the "swelling test" in the following manner. The meal (5 grams) is mixed with boiling water (50 c.c.) in a graduated cylinder and left for 2 hours, and the amount of clear liquid read off. Whilst meals prepared by the old process absorb the whole of the water added, those obtained after extraction with light petroleum only absorbed from 4·1 to 6·3 parts. As regards the feeding value of the meal, the percentage of fat and proteids are, of course, more important than the absorptive power for water. The method is, however, very useful for ascertaining the process by which the meal was made. N. H. J. M.

## Analytical Chemistry.

**Table of Factors.** By EDMUND H. MILLER and J. A. MATHEWS (*J. Amer. Chem. Soc.*, 1896, **18**, 903—904).—A convenient table for the conversion of the weights of precipitates of constant composition into the corresponding metal or oxide, or acid radicle. The logarithm is given in each case. L. DE K.

**Convenient form of Measuring-flask.** By WILHELM WISLICENUS (*Ber.*, 1897, **30**, 278. Compare this vol., ii, 70).—The flask described

by the author (*loc. cit.*) has been already introduced by Biltz (Abstr., 1896, ii, 671) and by Giles (Abstr., 1894, ii, 251). M. O. F.

**Some Extensions of the Plaster of Paris Method in Blowpipe Analysis.** By W. W. ANDREWS (*J. Amer. Chem. Soc.*, 1896, 18, 849—869).—The author has improved this well-known process by introducing a set of new reagents and by improving the material. A solution of iodine in potassium thiocyanate is now used to produce volatile iodides in place of hydriodic acid, whilst a mixture of potassium bromide and potassium hydrogen sulphate or phosphate is substituted for fuming hydrobromic acid. A mixture of potassium chloride, iodide, or fluoride with metaphosphoric acid is also found to be a useful reagent. To dissolve the films, the author now employs potassium cyanide solution rendered more stable by the addition of a little free alkali, whilst a solution prepared by boiling aqueous potash with excess of flowers of sulphur is substituted for yellow ammonium sulphide in order to dissolve the films and produce sulphide spots.

In order to produce coloured fluxes on the tablets, the material must be made more resistant to the dissolving effect of the metaphosphoric acid and of the alkali in the borax. The author advises adding a teaspoonful of boric acid to every quart of water used in making the plaster tablets.

The great delicacy of the plaster blowpipe assay is again proved by numerous instances. L. DE K.

**Effect of an Excess of Reagent in the Precipitation of Barium Sulphate.** By C. W. FOULK (*J. Amer. Chem. Soc.*, 1896, 18, 793—807).—The author has made a large number of experiments on the best way of precipitating barium sulphate, and tabulated the results.

It appears that when a barium salt is precipitated by sulphuric acid in the presence of hydrochloric acid, a large excess of the reagent is required, especially if the quantity of hydrochloric acid is very large. If the precipitate has to be collected at once, a very large excess of sulphuric acid should be added, as otherwise it would be necessary to leave the mixture for some time, stirring at intervals.

Barium sulphate obtained by the use of excess of sulphuric acid in the presence of hydrochloric acid is coarse and crystalline; that obtained by adding excess of barium chloride is finely divided and liable to run through the filter. The precipitation is not complete unless an excess of the reagent is added, particularly so if there is much hydrochloric acid present. The precipitate always contains occluded barium chloride which no amount of washing can remove; it may, however, be extracted from the precipitate after ignition by repeated treatment with boiling water and re-ignition. If the moist filter containing the precipitate is put into a platinum crucible, precipitate end up, and then gradually burnt, no reduction to sulphide takes place. L. DE K.

**Elementary Analysis under pressure in a Closed Vessel.** By WALTHER HEMPEL (*Ber.*, 1897, 30, 202—211).—The author proposes to carry out combustions of organic substances in compressed oxygen (25 kilos. to the square cm.) in a modified form of the Berthelot calorimetric bomb, which is made of such dimensions that it can be accurately

weighed (250 grams). After the combustion, which is carried out as in thermochemical determinations, the gases are allowed to escape slowly through the absorption tubes, and the bomb is then twice filled with pure air, and pumped out through the absorption tubes by means of a water pump. The amount of nitrous acid formed is determined by washing out the bomb (after it has been treated as above and weighed), with water, and titrating with centinormal alkali. Sulphur, if present, is entirely converted into sulphuric acid, which is estimated in the usual way. The amount of water formed is given by the increase in weight of the calcium chloride and sulphuric acid tubes which are used *plus* the increase in weight of the autoclave, *minus* the weight of acids formed. As the apparatus has to be exhausted, soda lime tubes are used for absorbing the carbonic anhydride.

A. H.

**Estimation of Arsenic, Antimony, and Foreign Metals in Commercial Copper by Electrolytic Methods.** By A. HOLLARD (*Compt. rend.*, 1896, **123**, 1063—1065).—When hydrogen sulphide is passed through the liquid from which the copper has been electrolytically removed, the precipitate may contain arsenic, antimony, lead, and perhaps traces of copper, whilst iron, nickel, and cobalt may be present in the filtrate. The sulphides of arsenic and antimony are separated from the other sulphides by solution in ammonium sulphide, the arsenic being eventually precipitated as magnesium ammonium arsenate, and the antimony reprecipitated as sulphide, the latter being dissolved in concentrated sodium sulphide solution, and the antimony deposited by electrolysis. From the filtrate from the hydrogen sulphide precipitate, the iron is removed as hydroxide, the nickel and cobalt being deposited electrolytically from an ammoniacal solution containing ammonium sulphate.

*Estimation of Silver.*—If the copper is rich in silver, the whole of the latter will be deposited with the copper, but if the amount of silver is but small, then the silver, in from 10 to 50 grams of the metal, is precipitated as chloride, dissolved in 2 per cent. potassium cyanide solution, and submitted to a current of 0·025 to 0·035 amp.

*Lead* may be estimated by electrolysing a nitric acid solution of the copper, the platinum cone being connected with the positive, and the spiral with the negative pole. At the end of 12 hours, the lead is entirely deposited on the cone as hydrated peroxide. The intensity of the current should be 0·3 amp.

A. C. C.

**Estimation of Thoria. Analysis of Monazite Sand.** By CHARLES GLASER (*J. Amer. Chem. Soc.*, 1896, **18**, 782—793).—Two grams of the finely pulverised mineral is heated with strong sulphuric acid, or fused with potassium hydrogen sulphate; on treating the fused mass with cold water, silica and tantalic acid are left undissolved, but must be freed from traces of thoria by repeated treatment with hydrofluoric and sulphuric acids; the thoria solution is then added to the main liquid. This is freed from titanium, &c., by treatment with hydrogen sulphide, first at the boiling heat and then in the cold. After filtering, the liquid is boiled to expel the gas, any excess of acid is neutralised with ammonia, and the thoria, together with other

metals of the cerium group, is precipitated by adding 100 c.c. of a saturated solution of ammonium oxalate previously heated to boiling.

The oxalates are next reduced to oxides by ignition, converted into sulphates, the greater part of the acid neutralised with ammonia, the solution heated to boiling, and hot ammonium oxalate solution added in excess; after a little while, a few c.c. of ammonium acetate is added. On cooling, the metals of the cerium group are precipitated as oxalates, leaving the thoria in solution; the latter can then be precipitated with ammonia, washed, ignited, and weighed.

The author also gives a detailed account of the estimation of titanic acid, tantalic acid, glucina, zirconia, and yttria, lanthanum and didymium oxides, cerium oxide, ferric oxide, lime, alumina, lead, silica, and phosphoric acid, all of which occur in the monazite sand.

L. DE K.

**Estimation of Aluminium in Phosphates.** By HENRI LASNE (*Bull. Soc. Chim.*, 1896, [4], 15, 237—248).—The author has studied sources of error in the different methods of analysing phosphates containing alumina. Methods involving the precipitation of alumina as phosphate in presence of ammonium acetate give erroneous results, on account of the variation of the composition of the precipitate and of the solubility of the alumina. The latter increases with the amount of acetic acid present, and vanishes when the solution is slightly ammoniacal. The amount of phosphoric acid in the precipitate increases with the quantity present in the solution.

In the case of aluminium phosphate precipitated in the presence of ammonium thiosulphate, it was found that the quantity of phosphoric acid in the precipitate increased with the quantity present in the solution up to a certain point, and then became fairly constant. A correction could be made for the loss of alumina due to solubility if the conditions were kept constant.

A sample of known composition was analysed by several different methods, of which the oxalic acid method alone gave satisfactory results.

M. W. T.

**Analysis of Aluminium.** By JAMES O. HANDY (*J. Amer. Chem. Soc.*, 1896, 18, 766—782).—The best solvent for commercial aluminium is a mixture of 100 c.c. of nitric acid of sp. gr. 1·42, 300 c.c. of hydrochloric acid of sp. gr. 1·20, and 600 c.c. of 25 per cent. sulphuric acid. One gram of aluminium borings is dissolved in 30 c.c. of the acid mixture, and the solution evaporated until dense fumes of sulphuric acid begin to appear; after cooling slightly, the residue is boiled with 100 c.c. of water and 10 c.c. of weak sulphuric acid, 1 gram of metallic zinc is added, and the whole heated for some time to precipitate the copper and reduce the iron to the ferrous state. The latter is then titrated with permanganate, whilst the copper, mixed with silica, is dissolved in dilute (15 per cent.) nitric acid, and titrated with potassium cyanide, after the addition of a slight excess of sodium carbonate. The undissolved silicon and silica are first fused with sodium carbonate, and afterwards recovered by evaporating with sulphuric acid; the result is finally calculated to silicon. Graphitic or crystalline silicon

may be estimated by dissolving 1 gram of the metal in 30 c.c. of dilute hydrochloric acid (1 : 2) in a platinum dish, and adding to the solution 2 c.c. of hydrofluoric acid, which dissolves the non-crystalline silicon, but does not attack the graphitic variety; after filtering, for which a funnel coated with paraffin must be used, the residue is ignited and fused with sodium carbonate and the silica estimated as directed above.

To estimate any sodium, 1 gram of the borings is dissolved in 50 c.c. of nitric acid with a sufficiency of hydrochloric acid; the solution is boiled to expel chlorine, evaporated in a platinum dish, and finally heated until no more nitric fumes are given off. The residue is then powdered, and treated as if it were an estimation of alkalis in a silicate, namely, by fusing with 1 gram of ammonium chloride and 8 grams of pure calcium carbonate, &c. Carbon and nitrogen are estimated by Moissan's method, slightly modified.

If it is desired to make a direct estimation of the aluminium, the following process is recommended. One gram of the sample is dissolved in 30 c.c. of dilute hydrochloric acid, evaporated to dryness, and the residue boiled with 10 c.c. of strong hydrochloric acid and 75 c.c. of water. After diluting to 250 c.c., hydrogen sulphide is passed through the solution, which is filtered, and the excess of hydrogen sulphide boiled off, the last traces being removed by adding 1 c.c. of strong nitric acid, and boiling for 10 minutes. When cold, the liquid is made up to 500 c.c., 50 c.c. is pipetted off, diluted to 250 c.c., heated to boiling, and a slight excess of ammonia added, the boiling being continued for 20 minutes. The alumina is collected, washed with boiling water, ignited, and weighed as quickly as possible, as, according to the author's experience, the precipitate is exceedingly hygroscopic.

The rest of the paper is devoted to the analysis of alloys of aluminium with copper, nickel, manganese, chromium, tungsten, titanium, zinc, tin, and phosphorus; also to the analysis of crude hydrated alumina and of bauxite, but, although containing useful details, the processes used, on the whole, present no novel features. L. DE K.

**Analytical Methods involving the Use of Hydrogen Peroxide.** By B. B. Ross (*J. Amer. Chem. Soc.*, 1896, **18**, 918—923).—Baumann has used hydrogen peroxide for the estimation of chromic acid and chromates; the latter, when mixed with a sufficiency of sulphuric acid and an excess of hydrogen peroxide, gives off 8 atoms of oxygen for every molecule of chromic acid, or 445·3 c.c. of oxygen for 1 gram of the acid.

The author, having repeated Baumann's experiments, has successfully applied the process to the indirect estimation of iron. After reducing the ferric compound to the ferrous state, an excess of standardised solution of potassium dichromate is added, and the undecomposed chromic acid is then estimated by means of hydrogen peroxide.

The author has tried to apply the process in sugar analysis. For this purpose, the sugar is inverted, and then boiled with alkaline copper tartrate solution; and the precipitated cuprous oxide, after being well washed, is boiled with dilute sulphuric acid and a known quantity of potassium dichromate, the excess of which is then estimated by the

hydrogen peroxide process. Although free from objection in theory, the practical results have, as yet, not been altogether satisfactory.

L. DE K.

**Reducing Action of Chloroform on Fehling's Solution.** By CHARLES G. MATTHEWS (*J. Fed. Inst. Brewing*, 1896, **2**, 333—334).—It is known that chloroform reduces Fehling's solution, and the author has made determinations of the amount of cupric oxide obtained by the ordinary gravimetric method, corresponding with known weights of chloroform. It is found that 1 c.c. of that substance gives 1·72 gram of cupric oxide, or that 1 gram gives 1·15 gram of cupric oxide. When, therefore, as is often the case, chloroform is added to a sugar solution which is to be analysed, it should be either expelled by boiling before the estimation of the sugar is undertaken, or its cupric-reducing power should be taken into account and a correction made. A. C. C.

**Estimation of Alcohol.** By H. DROOP RICHMOND (*J. Fed. Inst. Brewing*, 1896, **2**, 529—535).—In estimating the percentage of alcohol in a liquid indirectly, from the sp. gr. of the liquid itself and that of the non-volatile portion (extract) remaining after distillation, the sp. gr. of the distilled alcohol can be obtained, according to Tabarie, by dividing the sp. gr. of the liquid by that of the extract. It was subsequently pointed out by Blunt that more correct results were obtained if the sp. gr. of the extract (water = 1) were subtracted from that of the original liquid + 1. In this communication, the author demonstrates the theoretical accuracy of Blunt's method. A. C. C.

**A New Method for the Estimation of Glycerol.** By FRÉD BORDAS and SIG. DE RACZKOWSKI (*Compt. rend.*, 1896, **123**, 1071—1072).—The authors employ a slight modification of the process suggested by Nicloux for the estimation of small quantities of alcohol. A solution of potassium dichromate (48 grams per litre) is added to 5 c.c. of a dilute solution of glycerol containing 2 c.c. of sulphuric acid, until the dichromate is completely reduced, a very slight excess of the latter changing the colour of the liquid from a bluish-green to a yellowish-green. The glycerol solutions must not contain less than 0·1 gram or more than 2 grams per litre, since the colours are then either too faint or too intense. Every 1 c.c. of the above dichromate solution corresponds with 0·005 gram of glycerol. A. C. C.

**Estimation of Reducing Sugars in Terms of Copper Oxide.** By GEORGE DEFREN (*J. Amer. Chem. Soc.*, 1896, **18**, 749—766).—The author has reinvestigated the relation between copper oxide and anhydrous dextrose, maltose, and lactose, and has tabulated the results, the method employed being the same as that recommended by O'Sullivan (this Journal, 1876, ii, 130). The dextrose equivalent varied from 0·4401 to 0·4511; that of maltose from 0·7240 to 0·7433 and that of lactose from 0·6289 to 0·6430.

These differences are due to the influence of dilution, the equivalent becoming greater as the solution employed is more concentrated. The author has constructed a very useful and complete table for the benefit of sugar analysts, giving the empirical relation between percentage of

copper oxide obtained and the corresponding dextrose, maltose, and lactose. L. DE K.

**Estimation of the Ready-formed Sugars of Malt.** By G. HARRIS MORRIS (*J. Fed. Inst. Brewing*, 1896, 2, 224—237).—The method usually employed for the estimation of the ready-formed sugars of malt, consists in making a cold water extract of the malt, and then estimating the amount of total dissolved solid matter. From this number, the sum of the percentages of the soluble uncoagulable proteids, the ash, and the acid is subtracted, the difference being taken as representing the ready-formed sugars. The author has endeavoured to determine these sugars directly, both by fermentation and by ascertaining their cupric oxide reducing power, and expressing the results in terms of dextrose. He finds, however, that both of these methods give inaccurate results, and that the older method yields numbers which bear a fairly constant relation to the true sugars, as determined by the alcohol extraction method of C. O'Sullivan (Trans., 1886, 58). The following conclusions bearing on the above method are recorded. When ground malt is digested with water at 60°F., no diastatic action takes place during the first 3 hours. After this period, the starch granules are acted on, maltose being formed. At higher temperatures, diastatic action is more marked, although not very considerable, between 60°F. and 70°F. The more tender the malt, the greater is effect of temperature on this action. A. C. C.

**Invert-Sugar, I, II.** By JOHN HERON (*J. Fed. Inst. Brewing*, 1896, 2, 440—452, 457—482).—In Part I of this communication, a detailed account is given of the manufacture of invert-sugar, together with typical analyses of raw cane-sugar, and of invert-sugar.

In the second part, methods for the analysis of the commercial products are described which are considered by the author to give the most accurate results. A 1 per cent. solution of the mineral matter contained in such samples has, approximately, a sp. gr. = 1·008. In the estimation of the total organic solid matter in samples of sugar by the use of the 3·86 divisor, it is necessary, therefore, to estimate the amount of ash, and then to correct for its influence on the specific gravity of the solution. A. C. C.

**Composition and Fermentability of Fruit-sugar.** By KELHOFER (*Bied. Centr.*, 1896, 25, 760—761; from *Jahresber. Versuchs-Stat. Wädensweil*, 1895, 4, 93).—The original preparation known as fruit-sugar was a yellowish syrup containing 75 per cent. of sugar (dextrose and levulose), and therefore a suitable substitute for natural fruit-sugar. A substance similar in appearance to this, and containing the same amount of sugar, is now made, but the sugar consists of, for example, 39·45 percent. of invert-sugar and 34·75 percent. of cane-sugar. The more recent preparation, apart from being in the form of a syrup, has no advantage, when its greater cost is considered, over cane-sugar, either for effervescent liquids, food for bees, or as regards fermentability. N. H. J. M.

**Acidity of Milk increased by Boric Acid.** By E. H. FARRINGTON (*J. Amer. Chem. Soc.*, 1896, 18, 847).—The author has found that a

solution of boric acid in milk, shows about 4 times as much acidity as when the same amount of the acid is dissolved in water.

If, therefore, milk shows a high acidity, and is still fairly neutral to the taste, it may be safely assumed to contain boric acid.

L. DE K.

**Behaviour of the Resin Acids of Shellac in Gladding's and Twitchell's Processes for separating Fatty and Resin Acids.**—By FERDINAND ULZER and RUDOLF DEFRIS (*Zeit. anal. Chem.*, 1897, **36**, 24—27).—The resin acids of shellac behave, in Gladding's process (Abstr., 1882, 663), more like fatty acids than like those of pine resin, their silver salts being for the most part insoluble in ether. A dark sample of shellac, with the acid number 65·43, saponification number 204·78, and only 0·05 per cent. of unsaponifiable constituents, furnished 12·9 per cent. of "resin acid" by this method. Twitchell's process (Abstr., 1892, 389) consists in passing gaseous hydrogen chloride into an alcoholic solution of the acids, when fatty acids are converted into their ethylic salts, whilst resin acids remain free. After removal of the alcoholic hydrogen chloride by washing with water, the ethereal layer is dissolved in light petroleum and this solution shaken with soda, when the resin acids saponify. The above sample of shellac treated by this method yielded 66·56 per cent. of "resin acid," but at the same time a certain amount of an ethereal salt was produced having the saponification number 199·5. A second specimen yielded 72·89 per cent. of "resin acid."

M. J. S.

**Estimation of Fats, Soaps, and Fatty Acids in Animal Organs.** By CARL DORMEYER. (*Pfluger's Archiv*, 1896, **65**, 90—108. Compare, Abstr., 1895, ii, 540).—Renewed experiments confirm the author's previous conclusion that simple extraction of animal organs with ether is useless as a trustworthy method of estimating fats, soaps, fatty acids, or cholesterol. Even after a month's extraction, much fat remains undissolved. But after preliminary artificial gastric digestion, an additional amount of fat is extractable, averaging 8·5 per cent. of the total quantity.

W. D. H.

**Estimation of Free Fat in Soap.** By WM. WALTKE (*Chem. Zeit.*, 1896, **20**, 38).—Ten grams of the thoroughly dried sample is powdered in a mortar, introduced into a graduated 200 c.c. tube, and shaken with 100 c.c. of light petroleum free from moisture and non-volatile matters. The liquid is then poured off from the deposit through a filter, and 50 c.c. of the filtrate is evaporated in a weighed platinum dish, the residue being finally dried at 110°. The fat, should the least trace of moisture have been present, may contain some soap; to ascertain whether this is the case, it must be dissolved in a little light petroleum, when, if free from soap, it will yield a perfectly clear solution.

L. DE K.

**Estimation of the Percentage of Alkali and Fatty Acids in Soap.** By WM. WALTKE (*Chem. Zeit.*, 1896, **20**, 240).—A solution of 20 grams of the sample in about 100 c.c. of water, contained in a porcelain basin, is mixed with 70 c.c. of normal sulphuric acid, and heated until the fatty acids have completely melted. The

mixture is then cooled a little and rinsed by means of light petroleum into a 300 c.c. cylinder graduated to 0·25 c.c., and provided with a ground stopper, and a tap at the bottom. The aqueous layer should not occupy more than 200 c.c., and the petroleum layer not more than 100 c.c. After thoroughly shaking, the exact volumes of the two layers are carefully noted, and one-half of the top layer is pipetted off; after distilling off the light petroleum, the fatty acids are dried at 110° and weighed. The aqueous layer is now run off and the excess of acid titrated with normal soda. The amount of alkali in the soap is then easily calculated.

In some cases, where the use of light petroleum is inconvenient, on account of an emulsion being formed, the author employs either chloroform or carbon bisulphide; the aqueous layer then, of course, floats on the top. L. DE K.

**Estimation of Fibrin in Blood.** By A. KOSSLER and F. W. THEODOR C. PFEIFFER (*Zeit. anal. Chem.*, 1897, **36**, 70—71; from *Centr. inn. Med.*, 1896, 8.)—The method depends on the estimation of the nitrogen in equal volumes of the uncoagulated plasma and the defibrinated serum. The blood as it flows from the vein is mixed with about $\frac{1}{19}$th of its volume of a 4 per cent. potassium oxalate solution, and is then freed from blood corpuscles by centrifugal action. The nitrogen is estimated in a measured volume by Kjeldahl's process; another portion (20 c.c.) is caused to coagulate by the addition of 5 c.c. of a 2 per cent. calcium chloride solution. After some hours, the serum is pressed out from the clot with a glass rod, and when, by remaining liquid, it indicates that coagulation has ceased, it also is submitted to Kjeldahl's process. The result is multiplied by 25/20, to compensate for the dilution by the calcium chloride, and the difference between the two nitrogen determinations gives the fibrin nitrogen of the oxalate plasma. That of the original plasma is ascertained by Bleibtreu's method (Abstr., 1893, ii, 331; 1895, ii, 122). M. J. S.

**Detection of Glucase, the Enzyme of Maltose.** By MARTINUS W. BEYERINCK (*Bied. Centr.*, 1896, **25**, 753—757).—See this vol., ii, 183.

**Estimation of the Diastatic Capacity of Malt.** By ARTHUR R. LING (*J. Fed. Inst. Brewing*, 1896, **2**, 335—343). The method proposed by the author is a modification of Lintner's well-known method. Those tubes in the series in which the reduction is nearly complete are taken, and the amount of unreduced copper is determined by titration with a standard solution of dextrose containing 2 grams per litre. The exact number representing the diastatic capacity of the malt is thus more easily obtained than by making a second series of experiments with smaller quantities of the cold-water extract of malt. Satisfactory test-determinations are given. A. C. C.

# General and Physical Chemistry.

**Change of the Refractive Index by the Neutralisation, the Formation, and the Dilution of Solutions.** By GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1896, 21, 537—544).—The author endeavoured to determine whether the changes in the refractive index during the neutralisation of solutions are due to the changes in internal pressure, as it had been already proved that changes in volume and specific heat can be so explained (Abstr., 1895, ii, 204; 1896, ii, 289). The author deduces first the relation $\Delta n/\Delta v = -(n-1)$, where $n$ is the index of refraction, and $\Delta n$ and $\Delta v$ are the refraction and volume changes resulting from alteration of pressure. This relation is in accordance with the determinations of Hallwachs for changes in $n$ due to concentration changes, and with those of Pulfrichs on the formation of solutions. Electrolytic dissociation does not, however, as a rule, cause any change in the refractive index, except in the case of compounds containing hydrogen or hydroxyl ions. In these, the equivalent refraction of hydrogen increases by 1·8 on ionisation, and that of hydroxyl by 0·7, whilst the formation of ammonium from ammonia and a hydrogen ion is attended by an increase of 3·2 in the equivalent refraction.

L. M. J.

**Atomic Refractions of Carbon, Hydrogen, Oxygen, and the Halogens.** By ISIDOR TRAUBE (*Ber.*, 1897, 30, 39—42).—The atomic refractions calculated by Brühl for the $(\mu^2-1)/(\mu^2+2)$ formula are all higher than the true values, as no regard was paid to the influence of association of the molecules in the case of certain liquids, this influence being more especially marked in the case of the first members of the different series of homologous compounds. Omitting all cases in which association is known or suspected to occur, and recalculating Brühl's values, the numbers obtained are found to agree closely with those calculated by the author from the molecular volumes (this vol., ii, p. 85). In the following table, the atomic refractions for the D line are given, the numbers in the first column being those obtained from the molecular volumes, and those in the second column Brühl's corrected numbers.

| | | | | | |
|---|---|---|---|---|---|
| C | 2·88 | 2·70 | Cl | 6·11 | 6·04 |
| H | 0·905 | 0·99 | Br | 8·85 | 8·84 |
| O′ | 1·60 | 1·52 | I | 13·84 | 13·82 |
| O″ | ,, | 1·97 | F | 1·41 | 1·50 |
| $O_2$ | ,, | 1·58 | F | 1·60 | 1·83 |

The corresponding numbers for the $\mu - 1$ formula may be obtained by multiplying the above by 1·659.

H. C.

**Atomic Refractions of Nitrogen.** By ISIDOR TRAUBE (*Ber.*, 1897, 30, 43—47).—The author, in continuation of his work on the atomic refractions of the elements (see preceding abstract), has calculated from the molecular volume formula the atomic refraction of nitrogen in a large

number of nitrogen compounds. The atomic refraction of trivalent nitrogen in the amines, nitriles, and similar compounds is always the same, the mean value for the D line being 2·65. Nitrogen in the nitro-, nitroso-, azo-, oximido-, isocyanic, and ammonium compounds has a much higher atomic refraction, the mean value being 3·77. As the pentad nitrogen atom has a greater refraction than trivalent nitrogen, it may be that in these latter compounds the nitrogen is in every instance quinquivalent.

H. C.

**Spectrometric Determinations.** By JULIUS W. BRÜHL (*Ber.*, 1897, **30**, 158—162).—The author has directly determined the refractions of several organic compounds, and gives the following values for the molecular refractions for the $H_\alpha$ and Na lines calculated from the $(n^2-1)/(n^2+2)$ formula, and for the molecular dispersions $H_\gamma - H_\alpha$.

| | $H_\alpha$ | Na | $H_\gamma - H_\alpha$ |
|---|---|---|---|
| Ethylic ether, $Et_2O$ | 22·31 | 22·41 | 0·53 |
| Methylal, $CH_2(OEt)_2$ | 19·08 | 19·16 | 0·43 |
| Ethylic orthoformate, $CH(OEt)_3$ | 39·14 | 39·30 | 0·89 |
| Ethylic orthocarbonate, $C(OEt)_4$ | 49·69 | 49·89 | 1·09 |
| Hydrazine, $NH_2{\cdot}NH_2$ | 8·82 | 8·87 | 0·27 |
| Dimethylhydrazine, $NMe_2{\cdot}NH_2$ | 18·58 | 18·68 | 0·60 |
| Butylmethylamine, $NHMe{\cdot}C_4H_9$ | 28·61 | 28·76 | 0·76 |
| Butylmethylhydrazine, $NH_2{\cdot}NMe{\cdot}C_4H_9$ | 32·32 | 32·50 | 0·92 |

H. C.

**Hydrazine, Hydrogen Peroxide, Water.** By JULIUS W. BRÜHL (*Ber.*, 1897, **30**, 162—172).—The author has in a former paper (Abstr., 1896, ii, 162) advanced the view that oxygen in hydrogen peroxide and water is quadrivalent, and that the former compound has the constitution HO⁝OH. It is here shown that compounds of the type $R_2N{\cdot}NH_2$ and $R_2N{\cdot}OH$, in which R may be any radicle or hydrogen, do not behave like hydrogen peroxide. The molecular refractions of compounds of this type are found to be equal to the sum of the refractions of their constituents, whereas in the case of hydrogen peroxide this is not so, the observed refraction being much greater than that calculated.

H. C.

**Normal Rotatory Dispersions.** By PHILIPPE A. GUYE and P. A. MELIKIAN (*Compt. rend.*, 1896, **123**, 1291—1293).—The authors have determined the rotatory dispersions of a number of carbon compounds; the specific rotatory powers for the line D, and the specific rotatory dispersions, are given in the following table. With the possible exception of methylic lactate, all the liquids are composed of simple molecules, and all have normal rotatory dispersion.

| | Sp. gr. | t | $[\alpha]_D$ | $[\alpha]_{V-Z}$ |
|---|---|---|---|---|
| Propylene oxide | 0·820 | 23·5° | +1·10 | +1·02 |
| Propylic β-methyladipate | 0·978 | 16·5 | +2·19 | +2·39 |
| Ethylic β-methyladipate | 0·986 | 18 | +2·25 | +2·70 |
| Isobutylic β-methyladipate | 0·950 | 18 | +3·01 | +3·73 |
| Secondary amylic chloride | 0·851 | 23 | +3·13 | +3·32 |
| Phenylamylic oxide | 0·924 | 24 | +3·62 | +4·14 |

| | Sp. gr. | t | $[\alpha]_D$ | $[\alpha]_{V-Z}$ |
|---|---|---|---|---|
| Methylic β-methyladipate............ | 1·050 | 17° | + 3·64 | + 3·16 |
| Methylic 2 : 6-methyl-3-octanonate. | 0·950 | 16 | + 3·83 | ,, |
| Isopropylic β-methyladipate......... | 1·034 | 16 | + 6·54 | + 4·99 |
| Methylic lactate......................... | 1·080 | 16 | − 7·95 | − 4·33 |
| Methylic butyryllactate ...... ..... | 1·019 | 20 | − 38·68 | − 28·65 |
| Methylic acetyllactate ............... | 1·080 | 15 | − 48·60 | − 36·97 |

Although the specific rotatory dispersions are of the same order of magnitude as the specific rotatory powers, they are not proportional to them. C. H. B.

**Spectra of Argon.** By JOHN TROWBRIDGE and THEODORE W. RICHARDS (*Amer. J. Sci.*, 1897, [iv], **3**, 15—20; also *Phil. Mag.*, **43**, 77—83).—The present paper is preliminary to a more exhaustive study of the discharges of electricity through rarefied gases, by means of a storage battery of 10,000 cells, which will give an electromotive force of about 20,000 volts. The red glow of argon is readily obtained with a voltage of about 2,000, but not with much less; Crookes' estimate of 27,600 volts is evidently excessive. The introduction of a condenser between the terminals of the Geissler tube made no difference in the red glow as long as the connections were good and the condenser quiet. As soon as a spark gap was introduced, or the condenser began to emit the humming sound peculiar to it, the beautiful blue glow so characteristic of argon immediately appeared. If this light is examined by a revolving mirror, it is seen to consist of intermittent discharges. The battery charges the condenser to the potential necessary to produce a spark between the terminals of the spark gap; the discharge of this accumulated electricity is produced in the tube, and then the operation is repeated. The potential required certainly cannot be greater than 2,000 volts, the E.M.F. of the battery which will easily produce the blue glow.

The oscillatory discharge of the condenser is an important factor in producing the blue spectrum of argon, and the effect of the oscillatory discharge in producing the blue spectrum can also be shown by the use of an electrical machine. If the terminals of the tube containing argon are connected with the terminals of an electrical machine, the pure red spectrum is obtained. If a spark gap is interposed in such a manner that a condenser charged by the machine can discharge through the tube, the blue discharge immediately occurs; the condenser discharge oscillates through the gas.

When the tube containing argon at a suitable pressure is brought near a Hertz oscillator, giving a rate of about 115,000,000 oscillations per second, it immediately shows the blue colour. The unusual sensitiveness of an argon tube to oscillatory discharges indicates that it will be of great use in the study of wave-motions of electricity. The change of colour in the tube from red to blue is so marked that an argon tube reveals what is not shown in a conspicuous manner by other gases. The authors propose to call an argon tube fitted for the study of electrical waves a talantoscope. H. C.

**Multiple Spectra of Gases.** By JOHN TROWBRIDGE and THEODORE W. RICHARDS (*Amer. J. Sci.*, 1897, [iv], **3**, 117—120; also *Phil. Mag.*, **43**, 135—139).—Having shown (preceding abstract) that the con-

tinuous discharge of a high tension accumulator through argon produces the red spectrum, whilst the oscillatory discharge of a condenser produces the blue spectrum, the authors proceeded to determine whether the different spectra noticed in the case of other gases are primarily dependent on the electrical conditions which cause the gas to glow. With nitrogen, the two different spectra were obtained by varying suitably the electrical conditions of the discharge. With the continuous discharge, the channelled spectrum was obtained, but when the condenser was introduced, the channelled spectrum gave place to bright lines, already well known and mapped. This line spectrum corresponds with the blue spectrum of argon. Hydrogen under the influence of the continuous discharge gives a multitude of sharp lines, among which the four usual hydrogen lines, although present, are by no means especially prominent. A large capacity is required to change this spectrum into the familiar four-line spectrum which is comparable with the blue spectrum of argon. Each of the halogens gives two spectra, one with and one without the condenser. Helium gave a brilliant yellow glow under the influence of the continuous discharge, and a brilliant blue with the condenser discharge, but since the bright helium lines remained in each, and every other important line in the blue spectrum proved to be an argon line, it is evident that the oscillations produced no considerable effect on the helium. H. C.

**Potential Differences between Metals and Electrolytes.** By OTTO WIEDEBURG (*Ann. Phys. Chem.*, 1896, [ii], 59, 742—749).—A theoretical paper dealing with the determination of contact differences of potential between metals and electrolytes, and in answer to objections to the Lippmann-Helmholtz theory of capillary electrical phenomena. H. C.

**Experimental Investigations on the Electrolysis of Water.** By ALEXEI P. SOKOLOFF (*Ann. Phys. Chem.*, 1896, [ii], 59, 802—804).—Corrections to some of the tables in the author's former communication on this subject (Abstr., 1896, ii, 510). H. C.

**Electrolytic Behaviour of Solutions of some Salts and Acids in Methylic Alcohol.** By GIACOMO CARRARA (*Zeit. physikal. Chem.*, 1896, 21, 680).—In the communication by Zelinsky and Krapiwin (this vol., ii, 5) on the above subject, reference was omitted to the author's work on many of the compounds investigated (Abstr., 1896, ii, 511). L. M. J.

**Specific Heats of Gaseous Elements and their Atomic Constitution.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1897, 124, 119—125).—The author summarises the known facts with respect to the specific heats of the gaseous elements. He points out that there are four distinct cases, (1) where the ratio of the two specific heats is 1·66, and the molecules are generally believed to be monatomic; (2) where the ratio is 1·41, and the molecules behave as if they were diatomic and show no signs of dissociation into monatomic molecules, although at high temperatures there are indications that such dissociation is beginning to take place; (3) where the ratio is 1·30

(chlorine, bromine, and iodine) and the diatomic molecules dissociate more or less completely at high temperatures. In these cases, the ratio indicates that a considerable amount of internal work is done when the temperature of the gas is raised between ordinary limits; (4) where the ratio is 1·175 and the molecule is tetratomic, but becomes diatomic at high temperatures. The specific heats at constant volume are in the four cases 3·0, 4·8, 6·6, and 11·4, and the ratios of the three chief numbers are not far removed from 1 : 2 : 4. There is, therefore, some ground for supposing that the specific heats of elementary gases at constant volume are proportional to the number of atoms in their molecules. C. H. B.

**Variation of Melting Points with the Pressure.** By R. Demerliac (*Compt. rend.*, 1897, **124**, 75—77).—Between 1 atmosphere and 10 atmospheres, the variations in the melting points with variations in the pressure are, in the cases of paratoluidine and α-naphthylamine practically identical with those calculated by means of Clapeyron's formula. The author has also made experiments with a view of ascertaining whether this formula holds good at high pressures. In the case of benzene, observations were made between 10 and 450 atmospheres, and when the results are plotted with the rise in melting point for ordinates and the pressures for abscissæ, the curve is concave towards the axis of the pressures. The curve is a hyperbola, and beyond 330 atmospheres it becomes approximately parallel with the axis of the pressures, or, in other words, $dT/dp$ tends towards zero. In the case of paratoluidine, the curve is also a hyperbola, and $dT/dp$ tends towards 0 when $p$ increases beyond 180 atmospheres. α-Naphthylamine gives a curve of the same kind, and $dT/dp$ tends towards zero when $p$ exceeds 150 atmospheres. C. H. B.

**Thermochemical Method for the Determination of the Equivalents of Acids and Bases.** By Marcellin P. E. Berthelot (*Ann. Chim. Phys.*, 1896, [vii], 7, 283—288).—The author describes a thermochemical method by which the equivalent of an acid or a base may be determined, even if the composition of the compound is unknown. A given weight, $p$, of the acid is made up with distilled water to a given volume, say two litres; a known quantity of this solution, say 500 c.c., is then taken, 100 c.c. of potash of known strength (KOH = 2 litres) is added, and the heat evolved, $q_1$, is measured. A second 100 c.c. of the potash solution is added, and the heat evolved, $q_2$, is also measured, the operation being repeated until, on the addition of fresh alkali, no more heat is developed. The total heat of combination thus measured $(q_1 + q_2 + \ldots\ldots + q_n)$ is one-quarter of that which the given weight, $p$, of the acid would evolve. The equivalent, E, of the acid can then be obtained by the equation $E = \frac{2000}{400n} p = \frac{5p}{n}$, and is approximate to $1/n$th.

It is necessary that the amount of alkali added in the first instance should be insufficient to neutralise all the acid taken, otherwise $p_2$, $p_3$, &c., become 0. In order to determine the equivalent more accurately,

the experiments must be repeated, using the same strength of acid, but the potash only $\frac{1}{10}$th as strong; by this means the equivalent will be approximate to $\frac{1}{10}n$. The approximation can be made even closer by using more dilute solutions of potash.

In the case of monobasic acids, the numbers $q_1$, $q_2$, &c., are equal among themselves; in the case of many polybasic acids, however, these numbers differ considerably, decreasing, as a rule, with each fresh addition of alkali.

The same rules apply for the determination of the equivalent of a base, but in all cases the rules only apply to soluble acids or bases yielding soluble salts. Special precautions are necessary in the case of an insoluble acid, an insoluble base, or an insoluble salt resulting from a soluble acid and base. J. J. S.

**Thermochemical Relations between the different Modifications of Ordinary Glucose.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1896, [vii], 7, 51—57. Compare Béchamp, Abstr., 1894, ii, 2; Tanret, Abstr., 1895, i, 490).—The author gives the following thermochemical data at 20°.

| | D. Solution. | N. Heat evolved by the action of 5/2 NaOH on the Solutions. | D + N. |
|---|---|---|---|
| | Cal. | Cal. | Cal. |
| $\alpha$-Glucose ($\alpha_D = 106°$) ...... | − 2·15 | + 3·75 | + 1·45 |
| $\beta$-Glucose ($\alpha_D = 52·5°$) ...... | − 0·96 | + 3·96 | + 3·00 |
| $\gamma$-Glucose ($\alpha_D = 22·5°$) ...... | − 1·42 | + 3·75 | + 2·33 |

It is therefore to be inferred that

(1) The change of $\alpha$-glucose into $\beta$-glucose absorbs − 1·55 Calories.
(2) The ,, ,, $\gamma$-glucose ,, ,, ,, − 0·67 ,,

The differences are even less for the compounds in solution, in fact they fall within the limits of experimental error. J. J. S.

**Pressure Differences produced by Isothermal Distillation.** By MAX REINGANUM (*Ann. Phys. Chem.*, 1896, [ii], 59, 764—767).—Experiments of Askenasy are described in which a tube about 1 metre long was closed at one end (previously somewhat enlarged and funnel-shaped) with a plug of plaster of Paris, filled with water saturated with gypsum, and then placed in a vessel of mercury, the closed end uppermost. Evaporation of the water through the plaster plug took place, this being hastened as far as possible by keeping the surrounding atmosphere dry, and the mercury rose in the tube to heights (893 mm.!) which were greater than those of the barometer at the time. The author shows that, in cases of this kind, if $p$ is the vapour pressure of water at the surface level of the mercury, $p'$ the vapour pressure at the level of the plaster plug, so that $p - p'$ is the hydrostatic pressure of a column of water vapour of the height of the tube, the mercury should then rise to the height $H' = (p - p')/(p + p') \times s \times 691·6\ T$ cm., where $s$ is the specific gravity of mercury, and $T$ the absolute temperature at the time of the experiment. H. C.

**Vapour Pressure of Compounds of Calcium Chloride with Water.** By WILHELM MÜLLER-ERZBACH (*Zeit. physikal. Chem.*, 1896, 21, 545—555).—The vapour pressures were estimated by the method previously adopted (Abstr., 1896, ii, 295), and the following results were obtained.

| Compound. | Temp. | Vap. Pres. | V.P. / V.P. of Water. |
|---|---|---|---|
| $CaCl_2 + 4—6H_2O$ | 15·5° | 2·47 | 0·192 |
| | 16·7 | 2·83 | 0·20 |
| | 28·0 | 7·02 | 0·25 |
| $CaCl_2 + 2—4H_2O$ | 15·0 | 1·47 | 0·116 |
| | 33·0 | 5·98 | 0·16 |
| | 13·6 | 1·57 | 0·135 |
| $CaCl_2 + 1—2H_2O$ | 15·0 | 0·64 | 0·05 |

The results agree fairly well with Roozeboom's determinations, but the author does not find two modifications of the compound $CaCl_2 + 4H_2O$, which are stated by Roozeboom to exist. The capability of forming a plastic mass, possessed by some salts, such as calcium chloride, the author considers to be due partly to the absorption of moisture from the atmosphere, but more particularly to inherent plasticity of the salt. The redetermination of the vapour pressure of sulphuric acid gave results in accordance with those of Regnault, except in the case of a strong acid, the value 0·061 being obtained, in place of 0·074 for acid of sp. gr. 1·614 at 15°. L. M. J.

**Internal Friction of Mercury Vapour.** By ARTHUR A. NOYES and H. M. GOODWIN (*Zeit. physikal. Chem.*, 1896, 21, 671—679).—The internal friction of a gas is dependent on the mass and volume of the molecule, the mean velocity and the mean free path, and if the values for different gases are compared, the relation obtained is $\eta_1 : \eta_2 = m_1c_1/q_1 : m_2c_2/q_2$, where $\eta$ is the coefficient of friction $m$ the mass of the molecule, $c$ the mean velocity, and $q$ the cross section of the molecule or its sphere of action. At equal temperatures, however, $m_1c_1^2 = m_2c_2^2$, so that the relation reduces to $q_1 : q_2 = \eta_2/\eta_1 \cdot \sqrt{m_1/m_2}$, and comparisons of $q$ may be made. Experiments were made with mercury, carbonic anhydride, and hydrogen, under similar conditions and with the same apparatus, and the results obtained were: $\eta Hg/\eta CO_2 = 2·17$; $\eta Hg/\eta CO_2 = 2·08$; $\eta Hg/\eta H_2 = 4·04$. From these results, the ratios $q Hg/q CO_2 = 1·02$ and $q Hg/q H_2 = 2·48$ are obtained, so that the cross section, and hence probably the volume, of the monatomic mercury molecule is practically identical with that of the complex carbonic anhydride molecule, a fact which appears to indicate that in molecules the interatomic spaces are very small. The density of the mercury molecule is about 4·5 times greater than that of carbonic anhydride. L. M. J.

**Some Peculiarities of Solubility Curves.** By HENRI L. LE CHATELIER (*Zeit. physikal. Chem.*, 1896, 21, 557—560.)—If curves be constructed with melting points as ordinates and equivalent composi-

tion of the melted portion as abscissæ, maxima usually occur in the neighbourhood of points where the composition is that of a definite compound, whilst in certain cases, for instance, a mixture of lithium and potassium carbonates, the maximum is reduced to a point. Curves of this nature are given for this mixture and for alloys of aluminium-copper, tin-copper, and antimony-copper. Theoretical investigations show that, in general, the composition of the melted part is different from that of the mixture, and that points occur as maxima when the compound formed is not dissociated in the solution. L. M. J.

**Law of Contraction on Dissolving Sugar in Water.** By ALFRED WOHL (*Ber.*, 1897, **30**, 455—460).—The contraction $dv$ of a solution of $x$ grams of cane-sugar in a volume of water $V$ is best represented by the equation

$$\frac{dv}{V} = a \cdot \frac{x(l-x)}{V^2}$$

$$dv = a \cdot \frac{x(l-x)}{V}$$

$$a = \frac{dv \cdot V}{x(l-x)}$$

The most probable value of the constant $a$ being 0·00303.

It is possible therefore with sufficient accuracy to determine the contraction by means of the formula

$$dv = 0{\cdot}00303 \ \frac{x(l-x)}{1-\sigma x}$$

whence

$$\sigma = 0{\cdot}36965 = 1 - \frac{1}{s}$$

and therefore the specific gravity of the solution

$$s = \frac{(1-\sigma x)}{(1-\sigma x)^2 - 0{\cdot}00303\ x(l-x)}.$$

J. F. T.

**Rate of Reduction of Chromic Acid by Phosphorous Acid.** By GEORGES VIARD (*Compt rend.*, 1897, **124**, 148—151).—The author has determined the rate of interaction of chromic acid and phosphorous acid in solutions of various degrees of concentration. The change can be approximately represented by the equation $dx/dt = K(A-x)^4$, where A is the initial quantity of chromic acid and $x$ the quantity reduced in the time $t$. It follows that $t = \frac{1}{3}KA^3 \times A_3 - (A-x)^3/(A-x)^3$, and if $C = 3KA^3$, $(A-x)^3 = A^3/(1+Ct)$.

The value of C increases with the concentration of the solution; it also varies with the time in one and the same solution, and reaches a maximum when about half the chromic acid is reduced, afterwards diminishing regularly. In dilute solutions, the variations with the time are much less, and the observed and calculated values of $x$ agree much more closely. Curves plotted with $t$ as abscissæ and C as ordinates show the influence of dilution on the reaction, and if the curves are continued until they cut the axis of C, an initial value of C

is obtained, which differs from the initial velocity, $KA^4$, by a constant only. It can then be proved that the initial velocity varies according to a power of the concentration, the exponent being 1·4.

C. H. B.

**Classification of Chemical Elements.** By P. E. Lecoq de Boisbaudran (*Compt. rend.*, 1897, **124**, 127—130).—In the table previously given (Abstr., 1895, ii, 440), it is not necessary to place hydrogen at the bottom of each column. It may be placed below lithium only, but in the particular arrangement this would imply the existence of an unknown element below beryllium, and of negative elements below the other families. The latter are, in reality, represented by the three elements of high atomic weights, Bi, Pb, Tl. The changes in the atomic weights of Be, Li, $(?\beta)''$ and $(?\alpha)'$ show that if the elements were *below* N, C, and B, they would have negative atomic weights, which is inadmissible.

The author denotes by the term "bascule," the difference between the atomic weights of a pair of odd and even elements and their mean atomic weight, and he shows, amongst other things, that these bascules are at a minimum at the nodes (*loc. cit.*) This would not be the case if Mg – Na were placed on the same level as Si – Al and S – P.

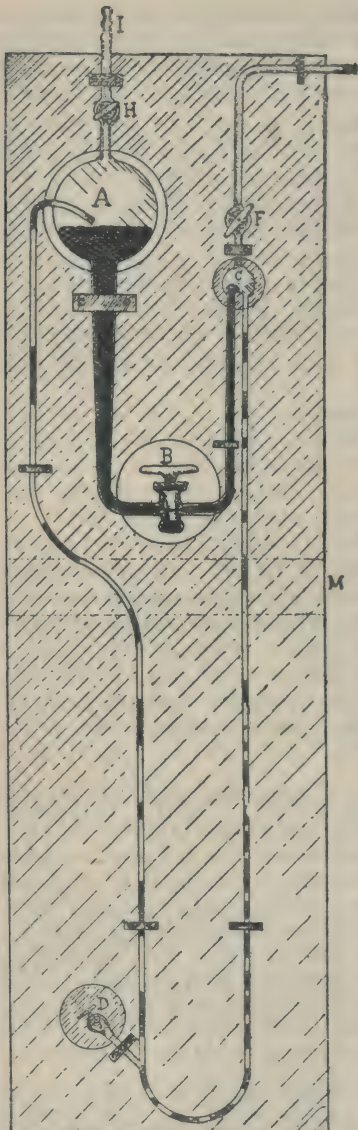
The bascule, Te – Sb, is greater than that of Sn – In, and the bascule $(?\zeta)''$ – I, seems to be greater than that of Ba – Cs. It follows that iodine occurs at the base of a high bascule and tellurium at the summit of another high bascule, and consequently the atomic weight of tellurium may be higher than that of iodine, although the mean of Te + Sb (124·25) may be lower than the mean of $(?\zeta)$ + I (129·95). The rule as to the progressive increase in atomic weights must be applied to the means of pairs of odd and even elements, and not to isolated elements.

C. H. B.

**Methods of Determining the Molecular Weights of Homogeneous Liquids.** By Isidor Traube (*Ber.*, 1897, **30**, 265—277).—The author gives a summary of all the methods at present available for the purpose of determining the molecular complexity of liquids (compare Ramsay, Abstr., 1895, ii, 40, and Linebarger, Abstr., 1896, ii, 9). In former papers, it has been shown that the molecular covolume for non-associated liquids is 25·9 at 15°. For the double molecule, the co-volume is 12·95, and, generally, if the co-volume has any value $y$, between 12·95 and 25·9, the association factor will be given by $x = 1 + \frac{25 \cdot 9 - y}{12 \cdot 95}$. This is the simplest of all methods for determining the value of the factor of association, as it is thus found from a single determination of the specific gravity. The author gives tables of the values of $x$ thus found and of the values obtained by other methods, showing the general agreement in the different cases.

H. C.

**A Simple Automatic Sprengel Pump.** By B. B. Boltwood (*Amer. Chem. J.*, 1897, **19**, 76—78).—In this pump (see the accompanying cut), the funnel of the ordinary Sprengel is replaced by a globe, A, provided with a tap, H, and a tube, I, which is connected with




a good water pump. The mercury, after passing C, falls down the vertical tube, and is swept up the left-hand branch by air, which is admitted at D, and in this way is returned to the globe, A, the action being thus rendered continuous.

A. H.

## Inorganic Chemistry.

**Conversion of Hypochlorites into Chlorates.** By Iyotibhushan Bhaduri (*Zeit. anorg. Chem.*, 1897, 13, 385—406).—When solutions of sodium hydroxide, of concentrations varying from 1·5 to 25 per cent., are treated with chlorine at 25—33°, very little chlorate is formed. The conversion of hypochlorite into chlorate is evident in solutions of 10 per cent., and in solutions above 20 per cent. the duration of the experiment has a great influence on the decomposition. Strongly alkaline solutions of sodium hypochlorite, if allowed to remain in the dark at 25—28° for some time, slowly decompose, yielding chlorate, sodium chloride, and oxygen; the decomposition is more pronounced when the solution is exposed to red light, and still more so when exposed to yellow light.

A solution of sodium hydroxide (5 per cent.) was saturated with chlorine, the excess of chlorine removed by a current of dry air free from carbonic anhydride, and an alkaline solution of sodium hypochlorite then gradually added until free chlorine was no longer present. This solution was very unstable, and in the course of an hour its titration factor altered greatly. After remaining in a closed flask in the dark for 3 hours, it was found that free chlorine was evolved, but on shaking the flask, this was again absorbed. It therefore appears that, under some conditions, sodium hypochlorite decomposes into chlorine and alkali.

When a solution of sodium hypochlorite is kept under diminished pressure, a regular evolution of oxygen takes place.

When solutions of sodium hypochlorite of various strengths are heated at 100° in sealed tubes in the dark for various periods of time, the percentage decomposition, in solutions in which the relative quantities of alkali, chloride, chlorate, and hypochlorite are the same, decreases with the dilution until a minimum is reached, and then, on further dilution, again increases; this point is reached when 1·6 per cent. of sodium hypochlorite is present. An aqueous solution of sodium hypochlorite is most stable, therefore, when the number of salt molecules in the solution is about 0·4 per cent. The amount of oxygen evolved after one hour is about $\frac{1}{4}$ to $\frac{1}{2}$ the amount in the chlorate which is formed. On further heating, the amount of free oxygen increases, but is never more than that contained in the chlorate. The relative amount of free oxygen increases with the dilution of the solution, and decreases with the rapidity with which the solution is heated. E. C. R.

**Hypoiodous Acid and Hypoiodites.** By ROBERT L. TAYLOR (*Chem. News*, 1897, **75**, 97).—The author confirms and extends Schönbein's observation. Aqueous solutions of iodine yield, in the presence of an alkali, a solution of potassium iodide and hypoiodite; whilst with silver salts and mercuric oxide, hypoiodous acid is formed; stronger solutions can be obtained by the use of iodine water with iodine in suspension. The solution from the alkali bleaches indigo strongly, but not litmus, that from the silver salts bleaches to a less extent, and that from the mercury only very feebly; but the latter can be rendered strongly bleaching by adding a small quantity of alkali. All the solutions are completely decomposed by boiling. D. A. L.

**Absorption of Hydrogen Sulphide by Melted Sulphur.** By H. PÉLABON (*Compt. rend.*, 1897, **124**, 35—37).—When sulphur and hydrogen are heated together in sealed tubes at 440°, hydrogen sulphide is formed and is absorbed by the molten sulphur, but is liberated as the latter solidifies, the phenomena being analogous to the "spitting" of silver. Hydrogen is not absorbed by liquid sulphur.

When hydrogen sulphide and sulphur are heated together, there is distinct absorption at 170°, but the quantity absorbed is much less than at 440°, and, in fact, between these limits it is higher the higher the temperature. Even boiling sulphur at ordinary pressure absorbs considerable quantities of the gas. The phenomena are very different from those of ordinary solution; at 440°, in a vacuum, the sulphur retains the whole of the absorbed gas, and only liberates it during solidification.

Hydrogen and sulphur begin to combine at 250°, but between this point and 350° combination is not complete. C. H. B.

**Density of Ozone.** By MARIUS OTTO (*Compt. rend.*, 1897, **124**, 78—81).—A glass flask was filled with oxygen and weighed, and afterwards filled with ozonised oxygen and again weighed. The ozone was next estimated by absorbing it in potassium iodide solution acidified with sulphuric acid. The result of two concordant experiments is that the density of ozone is half as high again as that of oxygen, or 1·6584. C. H. B.

**Action of Ammonia on Tellurium Tetrachloride: Tellurium Nitride.** By RENÉ METZNER (*Compt. rend.*, 1897, **124**, 32—35).—Tellurium tetrachloride is completely reduced by dry ammonia at 200—250°, with formation of ammonium chloride and liberation of nitrogen. At 0°, the chloride combines with the ammonia to form a yellowish compound, $TeCl_4,3NH_3$, which loses ammonia at the ordinary temperature, is decomposed by water with formation of tellurous acid, and by aqueous potash with evolution of ammonia. When heated, it blackens, gives off ammonia, and then a dark mixture of ammonium chloride and tellurous chloride volatilises.

If carefully dried ammonia is allowed to act on the chloride in a specially constructed apparatus, and the product is treated with liquid ammonia, washed repeatedly with this liquid, and finally with water, tellurium nitride, TeN, is obtained as an amorphous, friable, lemon-yellow compound. It detonates with great violence under percussion, or when heated to about 200°. It is not, however, decomposed by water nor by dilute acetic acid, but aqueous potash liberates all the nitrogen in the form of ammonia. C. H. B.

**Action of Hydrogen Sulphide and Hydrogen Selenide on Phosphorus Oxychloride.** By J. ADOLPHE BESSON (*Compt. rend.*, 1897, **124**, 151—153).—When hydrogen sulphide is dissolved in phosphorus oxychloride at 0°, and the solution is allowed to remain in a closed vessel, a yellowish-white, amorphous precipitate forms in about 24 hours, and after many weeks small, acicular crystals also separate. The amorphous product and the crystals have the composition $P_2O_2S_3$, and the former can be crystallised by dissolving it in phosphorus oxychloride in a closed vessel at 150°. When heated at 150°, the oxysulphide yields a sublimate of pentasulphide, and if heated in a vacuum at 200° for several hours, it completely decomposes into pentoxide and pentasulphide. It is slowly decomposed by water and moist air with liberation of hydrogen sulphide, burns in air or oxygen, and is violently oxidised by nitric acid.

If the solution of hydrogen sulphide in phosphorus oxychloride is heated at 100°, or, better, if the oxychloride is heated in a closed vessel with an open tube containing hydrogen persulphide, all the hydrogen sulphide is replaced by hydrogen chloride and the thio-oxychloride, $P_2O_2SCl_4$, is formed. It is a colourless liquid with a peculiar odour, and is slowly decomposed by water; it boils at 104° under a pressure of 10 mm. and at 119° under a pressure of 30 mm., and does not solidify at $-30°$. When heated in a vacuum at 300—350°, it yields a sublimate of phosphorus pentasulphide followed by one of the pentoxide, whilst a vitreous residue is left containing phosphorus, sulphur, and chlorine.

Hydrogen selenide has no action on the oxychloride at the ordinary temperature, but acts slowly at 100°, the products being brown phosphorus pentaselenide and metaphosphoryl chloride, $PO_2Cl$. The reaction is represented by the equation, $4POCl_3 + 5H_2Se = 10HCl + P_2Se_5 + 2PO_2Cl$. C. H. B.

**Action of Chlorine and Steam on Red-hot Carbon.** By ALEXANDER NAUMANN and F. G. MUDFORD (*Ber.*, 1897, **30**, 347—354)

—The primary reaction is represented by the equation $2Cl_2 + 2H_2O + C = 4HCl + CO_2$, and not, as Lorenz states (Abstr., 1896, ii, 17), by $Cl_2 + H_2O + C = 2HCl + CO$. Some carbonic oxide is undoubtedly formed, but this is due to a secondary action of carbon on the carbonic anhydride first formed, as is proved by the fact that the amount of carbonic oxide is increased when the layer of carbon is made longer, or the gases are passed more slowly through the heated tube. In the presence of excess of chlorine, a certain amount of carbonic oxide is oxidised to anhydride: $Cl_2 + H_2O + CO = 2HCl + CO_2$.

In the presence of excess of steam, no chlorine passes over unchanged, but some hydrogen is formed, and more of it in proportion as the temperature is higher, and the contact of the gases with the carbon of longer duration.

Lastly, it is pointed out that all these processes, resulting in the formation of hydrogen chloride, are exothermic, and that in consequence, when once the action is started, no further supply of external heat should be necessary; this is important from the point of view of a possible technical application of the processes. C. F. B.

**Helium.** By Marcellin P. E. Berthelot (*Compt. rend.*, 1897, **124**, 113—119).—The author has repeated his experiments on the action of a silent discharge on argon in presence of benzene, and confirms his earlier statements (Abstr., 1895, i, 412).

When helium is treated in the same way, there is not at first any luminous phenomenon visible by daylight, but after 11 or 12 hours' action of the discharge a characteristic orange luminescence appears and gradually increases in intensity. Its spectrum under atmospheric pressure shows the lines 587·5, 516·0 and 500·0 of helium, the line 546 of mercury, and the hydrocarbon band at about 426. After 17 hours' action of the discharge, with successive additions of small quantities of benzene, 13·7 per cent. of helium was absorbed, and this was increased to 16 per cent. in 39 hours. The product is a resinous solid similar to that obtained with argon.

Under similar conditions, but in presence of carbon bisulphide in place of benzene, helium is absorbed in the same way as argon. There is, however, no continuous luminescence, but only a "rain of fire" at the surface of contact of the gas and the mercury; some of the helium lines are shown, however. After 182 hours' action 55·5 per cent. of the helium was absorbed, and this was raised to 68·4 per cent. after 210 hours.

When the product is heated in a vacuum, helium is liberated, and after removal of carbon bisulphide and a trace of carbonic oxide (resulting from action on the glass), it again behaves in exactly the same way when subjected to the action of the discharge in presence of benzene.

The gas not absorbed in the first experiments even after prolonged action of the discharge, if brought in contact with fresh benzene and mercury and again subjected to the discharge, shows the characteristic luminescence, and is gradually absorbed.

Helium, like argon, is not affected by the action of the discharge in presence of mercury only. C. H. B.

**Artificial Colouring of Crystals of the Haloid Salts of the Alkali Metals by means of Sodium and Potassium Vapour.** By FELIX KREUTZ (*Ber.*, 1897, 30, 403. Compare Giesel, this vol., ii, 170). —A claim to priority. (See Kreutz, *Anz. Akad. Wiss.*, *Krakau*, April, 1892). M. O. F.

**Alkali Trihaloids.** By CHARLES H. HERTY and HOMER V. BLACK (*Amer. Chem. J.*, 1896, 18, 847—849. Compare Abstr., 1896, ii, 474).—An investigation to determine whether the mixed trihaloids of the alkali metals are isomorphous mixtures or true chemical compounds. The results obtained with rubidium dibromiodide confirm the latter supposition, the successive crops of crystals obtained from a solution of the ingredients in the requisite proportions being identical in composition. A. W. C.

**Action of Halogen Hydracids on Solutions of the corresponding Alkali Salts.** By ALFRED DITTE (*Compt. rend.*, 1896, 123, 1281—1283).—When hydrofluoric acid is added to a saturated solution of potassium fluoride, the solubility of the latter rapidly diminishes from 963 grams per 1000 grams of water to 324·6 grams per 1000 when 40·3 grams of hydrogen fluoride are present. From this point the solubility decreases very slowly with addition of more acid, reaches a minimum of 295·7 grams in 1000 when 113·6 grams of acid are present, and then increases somewhat rapidly as the proportion of acid increases. With sodium fluoride, the phenomena are similar, and the two curves have the same general character, although the actual quantity of salt dissolved is very much less. The minimum of 22·5 grams in 1000 is reached when 45·8 grams of acid is present. Analogous phenomena are observed with bromides and iodides, and they will be described in detail in a subsequent memoir. The numbers agree with Berthelot's calorimetric determinations which indicate the existence of more or less completely dissociated compounds of the salt and hydracid.

C. H. B.

**Action of Alkali Hydroxides on Solutions of the corresponding Halogen Salts.** By ALFRED DITTE (*Compt. rend.*, 1897, 124, 29—32).—When potassium hydroxide is added to a solution of potassium bromide, the solubility of the latter decreases as the proportion of the former increases. At first the curve is practically rectilinear, but afterwards the weight of bromide precipitated by a given weight of hydroxide diminishes as the total quantity of hydroxide present increases.

With sodium bromide, which can form a hydrate, the phenomena are different. The solubility of the bromide at first diminishes rapidly as the proportion of hydroxide increases, and then the rate of diminution becomes much slower, and between certain limits the total quantity of solid matter in solution remains constant. Finally, precipitation of the bromide again begins, and the solubility diminishes rapidly as the proportion of hydroxide increases. The curve seems to be formed of two distinct branches, one of which corresponds with a hydrated and the other with the anhydrous bromide.

Potassium chloride and iodide and sodium chloride, which do not form

hydrates, behave like potassium bromide. Sodium iodide and potassium fluoride, which do form hydrates, behave like sodium bromide, and give a curve with two parts. The intermediate section of the curve probably represents a condition of complex equilibrium in liquids containing both the hydrated and anhydrous salts. Even in solutions containing a large proportion of hydroxide, the curves give no indication of the formation of a compound of the hydroxide and the salt. C. H. B.

**Action of Hydrogen Chloride on Alkali Sulphates.** By ALBERT COLSON (*Compt. rend.*, 1896, **123**, 1285—1288).—Contrary to the general belief, sodium sulphate dried at 150° is attacked by dry hydrogen chloride at the ordinary temperature. When a large quantity of the sulphate is in contact with a small quantity of the gas, which corresponds with the maximum development of heat, the pressure of the gas after equilibrium has been established is independent of its mass. With 10 grams of the salt and 93 c.c., and 180 c.c., of gas, the pressures observed were

| | | | | | |
|---|---|---|---|---|---|
| t | 10° | 100° | 120° | 175° | 120° |
| p. | 2 | 15 | 23 | 77 | 24 mm. |

If the temperature is suddenly raised, the pressure developed is at first considerably higher than that properly corresponding with the temperature, but gradually returns to its normal value. This result is most probably due to the co-existence of several phases of the reaction and the superposition of one phase on another. The co-existence of several phases is due to the slowness with which equilibrium is reached and differentiates dissociation in multiple phases from dissociation in successive periods such as that observed by Isambert with ammonio-silver chloride.

With excess of sodium chloride in place of sodium sulphate (2·8 grams of sodium chloride and 1·8 grams of sulphuric acid), the pressures were also independent of the mass of hydrogen chloride present, and were as follows:

| | | | | |
|---|---|---|---|---|
| t | 0° | 8·2° | 37° | 100° |
| p. | 128 | 135 | 163 | 262—320 mm. |

With the system $NaHSO_4 + HCl = H_2SO_4 + NaCl$, the maximum pressure at 0° exceeds 2650 mm. In addition to this system, the phases in which the author imagines the reactions to take place and which correspond respectively to the pressures given above are, $Na_2SO_4 + 2HCl = H_2SO_4 + 2NaCl$ and $2Na_2SO_4 + 2HCl = 2HNaSO_4 + 2NaCl$. A fourth phase may result from the combination of sulphuric acid with the sodium hydrogen sulphate. C. H. B.

**Decomposition of Metallic Sulphates by Hydrochloric Acid.** By ALBERT COLSON (*Compt. rend.*, 1897, **124**, 81—84).—When excess of dry lead sulphate is brought in contact with dry hydrogen chloride, the pressure of the hydrogen chloride depends on the temperature, and is independent of the mass of the gas present. If the solid is afterwards treated with alcohol, sulphuric acid is dissolved, and hence it would seem that this acid is partially displaced by hydrogen chloride. It is possible, however, that the alcohol disturbs the conditions of equilibrium.

When dry hydrogen chloride comes in contact with dry cupric sul-

phate, the latter changes from white to yellow-brown. The pressure of the gas depends on the temperature, and not on the mass of gas present.

If lead sulphate is placed in a vessel of porous earthenware and treated with hydrogen chloride at 0°, and the salt is afterwards completely removed, it is found that the earthenware has absorbed a considerable quantity of sulphuric acid, which must therefore have been liberated. Similar results are obtained if the lead sulphate, after treatment with the gas, is squeezed between asbestos paper; the latter absorbs a considerable quantity of free sulphuric acid.

On the other hand, sulphuric acid does not decompose lead chloride at 15° in an atmosphere of hydrogen chloride. The tension of dissociation at 15° is less than half an atmosphere, and decomposition does not take place until the pressure is reduced.

The displacement of a volatile by a non-volatile acid of the same energy is not determined solely by the volatility of the displaceable acid, and, as a rule, heat or alteration of pressure is necessary in order to produce a change. The displacements is analogous to heterogeneous dissociations, and the maximum pressure at the ordinary temperature is usually less than one atmosphere.

In reversible chemical phenomena, as for saturated vapours, the heat developed, $L$, is connected with the absolute temperature, $T$, and the pressure, $p$, by the relation $L = T/425\,(u' - u)\,dp/dT$, $u'$ being the volume of 1 kilogram of the substance when completely volatilised, and $u$ the volume of the same mass condensed. C. H. B.

**Action of Lithium on Carbon and certain Carbon Compounds.** By ANTOINE GUNTZ (*Compt. rend.*, 1896, **123**, 1273—1275).—Lithium carbide, $C_2Li_2$, is formed when lithium is heated to redness in a vacuum with carbon, or when it is heated in a current of carbonic oxide or carbonic anhydride. In the latter case, the current of gas must be slow, so that the temperature does not rise above a dull red heat; at a bright red heat, very little carbide is formed. When the metal is heated in ethylene or acetylene, a mixture of carbide and hydride is formed, but methane has practically no action. If the nitride, instead of the metal, is heated with carbon, the carbide is mixed with a large proportion of cyanide, and the cyanide is also formed in considerable quantity when the metal is heated in a carbon dish in a current of nitrogen for the preparation of the nitride. C. H. B.

**Silver Hydride.** By EDWIN J. BARTLETT and WILLIAM F. RICE (*Amer. Chem. J.*, 1897, **19**, 49—52).—When hypophosphorous acid is added to silver nitrate solution, the mixture becomes wine-red, then black, and finally deposits a black, flocculent precipitate. If the precipitate is left in the solution, it is converted into metallic silver, but, on the other hand, if it is collected, washed, and dried at 60°, it consists of *silver hydride*; it loses 0·7 per cent. when ignited, metallic silver being left. The authors do not experimentally prove that the loss on ignition is due to hydrogen. A. H.

**Calcium Carbide; a new Reducing Agent.** By HENRY N. WARREN (*Chem. News*, 1897, **75**, 2—3).—The oxides of lead, copper, tin, iron, manganese, nickel, cobalt, chromium, molybdenum, and tung-

sten yield calcium alloys when heated with calcium carbide. The alloy in the case of lead is brittle and sonorous when struck, it melts at a lower temperature than pure lead, and acts less energetically towards water than lead alloys with the alkali metals. The presence of the calcium renders copper cold-short, and iron brittle and very oxidisable in contact with water. D. A. L.

**Action of Boron on Iron and Steel, and Errors in Iron Analysis caused by the Presence of Boron.** By HENRY N. WARREN (*Chem. News*, 1897, **75**, 91).—"Boron-eisen" can be obtained by melting ferric borate under a layer of borax; the compound obtained scratches flint; moreover, iron becomes contaminated with boron merely by heating the cast metal with fusible borates, or by reducing its oxide by means of carbon in the presence of a fusible borate; the amount of boron thus entering into combination amounting to from $\frac{1}{2}$ to 2 per cent. D. A. L.

**Action of Dissolved Carbonic Anhydride on Iron.** By PAUL PETIT (*Compt. rend.*, 1896, **123**, 1278—1280).—When water containing 638 milligrams of calcium carbonate per litre dissolved in carbonic anhydride, but neutral to phenolphthalein, is brought in contact with finely powdered iron, more than half the carbonate is precipitated, and iron is dissolved. Water saturated with carbonic anhydride will dissolve as much as 500 milligrams of iron per litre, with liberation of an equivalent quantity of hydrogen. The iron is converted into ferrous carbonate, and if the solution is exposed to air, ferric oxide is precipitated.

The water of the Moselle was found to dissolve 3·15 milligrams of iron per litre; if previously treated with a current of carbonic anhydride for a few minutes, it dissolved 200·6 milligrams; but if mixed with lime-water until slightly alkaline to phenolphthalein, it dissolved no iron at all.

Water containing about 0·1 gram per litre of calcium chloride, sodium chloride, potassium sulphate, or calcium nitrate, but no carbonic anhydride, dissolved only minute traces of iron, although a notable amount of iron was oxidised, sodium chloride being most active, and potassium sulphate coming next. If the solutions are saturated with carbonic anhydride, the quantity of iron oxidised but not dissolved remains practically the same, but the quantity of iron dissolved in each case is considerable, and is decidedly largest with potassium sulphate, the same with the sodium chloride solution as with water, less with calcium chloride, and considerably less with calcium nitrate. The potassium sulphate solution becomes alkaline, and the residue contains iron sulphide. With this exception, the action peculiar to each salt is independent of the presence of carbonic anhydride.

When air has access to the solutions, the quantity of iron dissolved remains practically the same, but the quantity of iron oxidised increases enormously. C. H. B.

**Action of Water of the Hubb Coal Mine on Cast Iron.** By FRANK W. DURKEE (*Amer. Chem. J.*, 1896, **18**, 849—858).—Cast iron for some time submerged in the water of the mine was found to have become changed to a mass resembling graphite, and soft enough to be

easily cut with a knife. Analyses of the original and of the transformed cast iron showed that the latter had lost considerably in percentage of iron and gained in oxygen.

The presence of ferrous sulphate in the water of the mine is accounted for by supposing that the iron pyrites in the coal has been acted on by moist air, and the sulphuric acid thus formed has attacked the cast iron, thus accounting for the loss of iron.

The oxide of iron found in the transformed cast iron is supposed to be due to a secondary chemical action, whereby the oxygen of the air dissolved in the water had attacked the original cast iron.

A. W. C.

**Pure Carbide of Iron.** By EDWARD D. CAMPBELL (*Amer. Chem. J.*, 1896, **18**, 836—847).—Carbide of iron prepared by a method differing but slightly from that used by Arnold and Read (Trans., 1894, 788) was found on analysis to have the formula $CFe_3$; this carbide is soluble in hot, moderately concentrated hydrochloric acid, the gaseous products being hydrogen, butane, and probably ethane, butylene, and dibutylene. The probability of the existence of a series of ferrocarbons, with a general formula $C_nFe_{3n}$, analogous to the olefine series of hydrocarbons, is also discussed. A. W. C.

**Volatility of Ferric Chloride.** By HENRY P. TALBOT (*Amer. Chem. J.*, 1897, **19**, 52—59).—When a solution of ferric chloride is evaporated to dryness and the residue heated at 130° for 2 hours, no perceptible volatilisation of the salt occurs. If, however, an ammonium salt is present, or if the iron salt is evaporated with aqua regia, a slight loss does occur. A. H.

**Silicide of Chromium.** By GUILLAME J. L. DE CHALMOT (*Amer. Chem. J.*, 1897, **19**, 69—70).—When chromium sesquioxide, charcoal, and excess of silica are heated in the electric furnace, a crystalline *chromium silicide*, $Si_2Cr$, is produced. It occurs in long, grey needles, and is attacked by hydrofluoric acid. The product cannot easily be obtained free from silicon. A. H.

**Reduction of Wolframite by Carbon in the Electric Furnace.** By ED. DEFACQZ (*Compt. rend.*, 1896, **123**, 1288—1290).—Wolframite was mixed with 14 parts of sugar charcoal for 100 parts of the mineral and heated in an electric furnace for 12 minutes with an arc of from 950—1000 ampères and 50 to 60 volts. The metallic product contained 92·59 per cent. of tungsten and 5·08 per cent. of carbon, with some iron and silica. The slag consisted chiefly of calcium oxide with 10·75 per cent. of tungstic anhydride and some ferric oxide and silica. Neither the metal nor the slag contained manganese, although the original wolframite contained 15·9 per cent. of this element. C. H. B.

**Recovery of Uranium from Residues.** By A. GAWALOWSKI (*Zeit. anal. Chem.*, 1896, **35**, 678).—The author has improved his method (Abstr., 1877, i, 345) by replacing the ammonium carbonate by sodium carbonate (commercial ammonia soda), which is both cheaper and more efficient as a solvent for uranium phosphate. The bulk of the phosphoric acid is removed from the solution by adding ferric

chloride, and the remainder by adding magnesia mixture as long as it produces turbidity. The filtrate from the magnesia precipitate may either be acidified at once with acetic acid, or the uranium can be precipitated by adding hydrochloric acid, boiling off carbonic anhydride, and then adding excess of ammonia. M. J. S.

**Alums of Vanadium Trioxide.** By AUGUSTO PICCINI (*Zeit. anorg. Chem.*, 1897, 13, 441—446; also Abstr., 1896, ii, 304).—*Potassium vanadium alum*, $K_2V_2(SO_4)_4 + 24H_2O$, is obtained in a similar manner to the alums previously described. It crystallises in transparent, greenish-violet crystals belonging to the cubic system. It is very easily soluble in water, crystallises only from the syrupy solution when cooled to 0—10°, and melts in its water of crystallisation at 20°, forming a green liquid; at the ordinary temperature, over sulphuric acid, it gradually loses part of its water; at 100°, it loses 35 per cent.; and becomes anhydrous at 230°. Sp. gr. = 1·782 at 4°/20°.

*Thallium vanadium alum*, $Tl_2V_2(SO_4)_4 + 24H_2O$, crystallises in pentagonal hemihedric or dyakisdodecahedric, reddish-violet crystals belonging to the cubic system. It is very easily soluble in warm water, somewhat less so in the cold. The crystals gradually alter when exposed to the air, and behave like the preceding salt when heated, becoming anhydrous at 230°, and leaving a yellowish-green residue. Sp. gr. = 2·342 at 4°/20°.

*Sodium vanadium alum*, $Na_2V_2(SO_4)_4 + 24H_2O$, crystallises from its syrupy solution at 0° in octahedra, and melts in its water of crystallisation at 9°.

The author gives a table of the specific gravities and solubilities of the vanadium alums and the refractive indices of the crystals.

E. C. R.

**An Experiment with Gold.** By M. CAREY LEA (*Zeit. anorg. Chem.*, 1897, 13, 447—448; also *Am. J. Sci.*, [iv], 3, 64).—A beautiful green solution is obtained when a 10 per cent. solution of sodium hypophosphite is mixed with 1 c.c. of a gold chloride solution (10 c.c. = 1 gram of gold) and a drop of sulphuric acid; as soon as the solution begins to darken, 30 c.c. of water is added. This solution becomes gradually turbid, and a bluish-black precipitate of metallic gold is deposited. After filtration, the green filtrate again becomes gradually turbid, and this phenomenon can be observed many times. The green coloration is due to the presence of finely divided metallic gold precipitated in the blue modification; and if the solution is shaken and allowed to remain, a precipitate of gold is obtained on the sides of the containing vessel which is yellowish-brown by reflected light and bright blue by transmitted light. E. C. R.

**Action of Phosphorus on Platinum.** By A. GRANGER (*Compt. rend.*, 1896, 123, 1284—1285).—When platinum is heated in phosphorus vapour in a current of carbonic anhydride at a temperature sufficient to start and maintain the action, the product is a greyish-black, lustrous, friable mass of the phosphide $Pt_3P_5$ described by Clarke and Joslin (Abstr., 1884, 400). Contrary, however, to the statement of these observers, the author finds that this phosphide is

completely soluble in aqua regia if the action is sufficiently prolonged. At high temperatures, a product is obtained which approximates in composition to PtP, and at a bright red heat the product retains only 4 per cent. of phosphorus.

When spongy platinum is used, the action takes place below a red heat, and the product is then the diphosphide $PtP_2$. Contrary to Schrötter's statement, the author finds that this compound is not completely soluble in aqua regia, and the part that dissolves has exactly the composition $Pt_3P_5$. C. H. B.

## Mineralogical Chemistry.

**Igneous Rocks from Smyrna and Pergamon.** By HENRY S. WASHINGTON (*Amer. J. Sci.*, 1897, [iv], 3, 41—50).—Several andesitic rocks from near Smyrna and Pergamon, in western Asia Minor, are described; analyses are given of the following. I, augite-andesite from Mount Pagos, south of Smyrna; the fresh rock is dark grey, with numerous phenocrysts of labradorite, augite, and fewer of biotite, in a hyalopilitic ground-mass consisting of microlites of labradorite and orthoclase and a colourless glass; sp. gr. 2·640. II, augite-andesite from Kara Tash, west of Smyrna; this is a very dark, compact rock with numerous small labradorite, and few augite and biotite, phenocrysts in an almost black, highly vitreous ground-mass; sp. gr. 2·601. III, biotite-dacite from Pergamon; when fresh, this a dark grey rock with numerous phenocrysts of labradorite, biotite, hornblende, and some of sanidine, in a fine-grained or vitreous ground-mass; sp. gr. 2·525; here, although no quartz is present, the silica is high enough for the rock to be called a dacite.

| | $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MgO. | CaO. | $Na_2O$. | $K_2O$. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|
| I. | 60·68 | 16·19 | 5·37 | 1·58 | 2·96 | 5·88 | 3·11 | 3·95 | 0·98 | 100·70 |
| II. | 61·93 | 18·47 | 1·93 | 2·23 | 2·66 | 4·31 | 2·92 | 3·92 | 2·28 | 100·65 |
| III. | 63·17 | 17·15 | 2·84 | 1·31 | 2·17 | 4·17 | 3·08 | 4·19 | 2·51 | 100·59 |

The rocks are compared with other volcanic rocks from western Asia Minor. L. J. S.

**Missourite, a new Leucite Rock from Montana.** By WALTER H. WEED and LOUIS V. PIRSSON (*Amer. J. Sci.*, 1896, [iv], 2, 315—323).—The Highland Mountain consists of an extinct group of greatly eroded volcanoes rising out of the plains of central Montana. The granular rock here described forms the irregular core or stock, $2\frac{1}{2}$ miles long, of one of these denuded volcanic centres; it is situated at the head of Shonkin Creek, on the north side of the mountains. The freshest and coarsest-grained rock is dark grey, with a mottled appearance, much resembling a coarse-grained gabbro; it has the following percentage mineralogical composition:

| Iron ore. | Augite. | Olivine. | Biotite. | Leucite. | Analcite. | Zeolites. |
|---|---|---|---|---|---|---|
| 5 | 50 | 15 | 6 | 16 | 4 | 4 |

The structure is granular, but is wholly allotriomorphic; iron ore, apatite, and olivine have been first formed, whilst the leucite and augite have crystallised contemporaneously.

Leucite, separated from the powdered rock by means of a heavy liquid, gave analysis I, this agrees with the usual formula $KAl(SiO_3)_2$; average sp. gr. 2·44.

Analcite and a new zeolite have been formed by the alteration of the leucite. The small portion of the powdered rock which floated in liquid of sp. gr. 2·30 gave analysis II; it consists of a minute intergrowth of two minerals, one isotropic and probably analcite, the other with weak double refraction which, as shown by the analysis, is probably a potassium zeolite of the natrolite type. Deducting from II the constituents of analcite, the figures under III are obtained; these agree approximately with the formula $(K_2,Ca)Al_2Si_3O_{10} + 2H_2O$, which is like that of natrolite, but with potassium and calcium in place of sodium; a potassium zeolite would be the expected result of the alteration of leucite.

| | $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | MgO. | CaO. | $K_2O$. | $Na_2O$. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|---|---|---|
| I. | 54·46 | 22·24 | 0·68 | trace | 0·10 | 18·86 | 0·70 | 2·29 | 99·33 |
| II. | 50·18 | 25·07 | trace | — | 1·70 | 8·36 | 6·53 | 9·02 | 100·86 |
| III. | 45·85 | 26·07 | — | — | 3·12 | 15·35 | — | 9·61 | 100·00 |
| IV. | 46·06 | 10·01 | 3·17 | 14·74 | 10·55 | 5·14 | 1·31 | 1·44 | |

| | FeO. | $TiO_2$. | $P_2O_5$. | MnO. | BaO. | SrO. | $SO_3$. | Cl. | Total (less O for Cl). |
|---|---|---|---|---|---|---|---|---|---|
| IV. cont. | 5·61 | 0·73 | 0·21 | trace | 0·32 | 0·20 | 0·05 | 0·03 | 99·56 |

The bulk analysis of the rock by E. B. Hurlburt is given under IV; this is compared with analyses of a leucite-basalt, absarokite of Iddings, and shonkinite (Abstr., 1896, ii, 192). Here there is about the same silica percentage as in shonkinite, but there is more potassium, so that leucite has been formed instead of orthoclase. Leucite has not before been described as a constituent of a granular, plutonic rock. L. J. S.

**Composition of Hawaiian Soils and Rocks.** By Albert B. Lyons (*Amer. J. Sci.*, 1896, [iv], 2, 421—429).—Several analyses are given of fresh and weathered volcanic rocks, and of the soils derived from these. I is the mean of 9 analyses of fresh lavas (the silica extremes are 35·86 and 58·06). II the mean of 3 analyses of tufa; this consists essentially of fragments of lava, more or less weathered, with also some fragments of coral limestone, &c. III is the mean of 3 analyses of "rotten" (weathered) lava. IV the mean of 10 analyses of soils; here the material was boiled for 2 hours in hydrochloric acid of sp. gr. 1·15, and the percentages are calculated from the weight of the ignited material. By this method, the insoluble residue consists almost wholly of silica and titanic anhydride, but contains some insoluble alkali silicates. I a, &c., are the same analyses calculated on the assumption that the $Al_2O_3$, and all the iron, as $Fe_2O_3$, have remained constant; this shows that there has been a considerable loss of silica, as well as of the more soluble constituents.

| | I. | II. | III. | IV. | Ia. | IIa. | IIIa. | IVa. |
|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 47·86 | 41·79 | 21·32 | 40·00 | 1680 | 1393 | 320 | 800 |
| $TiO_2$ | 3·63 | — | 7·33 | | 128 | — | 110 | |
| $Al_2O_3$ | 15·05 | 14·02 | 32·81 | 22·59 | 1000 | 1000 | 1000 | 1000 |
| $Fe_2O_3$ | 8·59 | 14·69 | 33·92 | 30·05 | | | | |
| FeO | 4·46 | 1·11 | 2·31 | | 156 | 37 | 35 | not est. |
| MnO | 0·50 | 0·29 | 0·30 | 0·21 | 18 | 10 | 5 | 4 |
| CaO | 8·62 | 10·55 | trace | 1·26 | 303 | 352 | — | 22 |
| MgO | 6·08 | 10·73 | 0·58 | 1·19 | 213 | 358 | 9 | 20 |
| $Na_2O$ | 4·22 | 1·99 | 0·47 | 0·50 | 148 | 66 | 7 | 9 |
| $K_2O$ | 1·07 | 0·91 | trace | 0·43 | 37 | 30 | — | 8 |
| CuO | 0·19 | 0·09 | 0·30 | — | 7 | 3 | 5 | not est. |
| $P_2O_5$ | 0·65 | 0·67 | 0·42 | 0·68 | 23 | 23 | 6 | 12 |
| $SO_3$ | 0·10 | 0·13 | 0·42 | 0·22 | 4 | 4 | 6 | 4 |
| $CO_2$ | — | 3·29 | — | — | — | — | — | — |
| S | 0·11 | — | — | — | — | — | — | — |

L. J. S.

[The Sacramento Mountains Meteorite.] By Warren M. Foote (*Amer. J. Sci.*, 1897, [iv], 3, 65—66).—This iron, which has been found in the Sacramento Mountains, Eddy Co., New Mexico, weighs 237 kilos., and measures 80 × 60 × 20 cm. On the surface are the usual characteristic markings and pittings, and the Widmanstätten figures are exceptionally regular and distinct. The latter distinguish this iron from the El Capitan iron, found in 1893 about 90 miles north of the Sacramento range. As there is an entire absence of surface alteration the iron must have fallen at a comparatively recent date, and it is probably the meteor seen to fall in 1876. Analysis gave Fe, 91·39; M, 7·86; Co, 0·52; Total, 99·77. L. J. S.

[Water] from Chichan-Kanab, Yucatan. By Jas. Lewis Howe, and H. D. Campbell (*Amer. J. Sci.*, 1896, [iv], 2, 413—415).—The Chichan-Kanab (little sea) is an almost unknown lake, over 6 leagues in length, in the interior of the peninsula of Yucatan. Water from near the shore of the lake gave analysis I, in grams per litre; that from the centre of the lake gave II.

| | Ca. | Mg. | K. | Na. | $SO_4$. | Cl. | $H_2S$. |
|---|---|---|---|---|---|---|---|
| I. | 0·865 | 0·313 | 0·025 | 0·301 | 3·361 | 0·368 | — |
| II. | 0·600 | 0·325 | 0·019 | 0·533 | 2·607 | 0·362 | 0·0495 |

The water near the shore is thus richer in calcium sulphate than that at the centre of the lake. Samples of material from the shores of the lake consist of gypsum. L. J. S.

## Physiological Chemistry.

The Causes of Absorption of Oxygen by the Lungs. By J. Lorrain Smith and John S. Haldane (*Proc. physiol. Soc.*, 1896—1897, 16).—The normal oxygen tension of arterial blood varies from 35 to 66 per cent. of an atmosphere in different animals, but is nearly always higher than that in the alveoli. It rises and falls with rise and fall of the oxygen tension of the inspired air. It falls with a fall of body temperature. When the oxygen supply of the body is in-

sufficient, the oxygen tension of the blood leaving the lungs rises relatively to that of the alveolar air and may become three or four times as high. Assuming that hæmoglobin has the same properties inside and outside the body, the symptoms caused by diminished atmospheric pressure, or deficiency of oxygen in the inspired air, are not due to the hæmoglobin passing through the lungs being insufficiently saturated with oxygen. W. D. H.

**Elimination of Water and Carbonic Anhydride from the Skin.** By WAKELIN BARRATT (*J. Physiol.*, 1897, 21, 192—208; *Proc. physiol. Soc.*, 1896—1897, 10—12).—The output of carbonic anhydride from the skin is small compared with that of water; the ratio for the upper limb at 35° is 1 : 200. There are variations from day to day, and from hour to hour. At 35°, the elimination of carbonic anhydride is greater than at 25°; the effect of temperature on the elimination of water is not marked.

The application of a ligature to the limb causes an increase in the carbonic anhydride and a decrease in the water eliminated.

W. D. H.

**Influence of Great Altitude on the Formation of Hæmoglobin.** By J. WEISS (*Zeit. physiol. Chem.*, 1897, 22, 526—527).—The experiments were made on rabbits at Andermatt and Pilatus. Control experiments were carried out on animals of the same litters kept at Basle. There was an increase in the number of corpuscles (from 12—24 per cent.), but none in the hæmoglobin. There is no ground for attributing a beneficial influence of high altitudes to the assimilation of iron and formation of hæmoglobin. W. D. H.

**Influence of Inanition on the Bones and Teeth.** By HUGO WEISKE (*Zeit. physiol. Chem.*, 1897, 22, 485—499).—The experiments were made on rabbits. After starvation, there is a slight loss of weight in the bones, which falls equally on their organic and inorganic constituents. In the teeth, on the other hand, the loss falls principally on their organic constituents. W. D. H.

**A Diffusion Apparatus.** By E. WAYMOUTH REID (*J. Physiol.*, 1897, 21, 85—100).—The apparatus described and figured is for the purpose of determining the relative diffusibilities through parchment paper of substances (glucose and peptone) normally absorbed in the intestine under conditions of temperature, pressure, &c., analogous to those in the body. These experiments were made with a view of comparing the numbers with those obtained in the gut of the living animal. The same paper can be used over again for glucose, but proteid solutions affect its permeability. Grübler's peptone is twice as diffusible as Witte's, and glucose is 3·74 times more diffusible than Grübler's peptone. W. D. H.

**Amount of Nucleon in Human Muscles.** By MARTIN MÜLLER (*Zeit. physiol. Chem.*, 1897, 22, 561—566).—The amount of nucleon (phosphorcarnic acid) found in the muscles of human adults in these experiments was 0·11, 0·13, and 0·22 per cent. It is less in the muscles of the new born; in five experiments, the results were: 0·04; 0·06; 0·02; 0·00; and 0·01 per cent. W. D. H.

**Influence of Fat in the Food on Milk.** By HENRY WING (*Ann. Agronom.*, 1896, **22**, 94—95; from *Cornell Univ. Agric. Exp. Stat. Bulletin*, 1895).—The addition of fat to the fodder of cows increases neither the quantity of milk secreted nor the amount of fat in the milk.

W. D. H.

**Amount of Nucleon in Cow's, Human, and Goat's Milk.** By KARL WITTMAACK (*Zeit. physiol. Chem.*, 1897, **22**, 567—574).—In cow's milk, the percentage of nucleon (phosphorcarnic acid) averaged 0·056; in human milk, 0·124; in goat's milk, 0·11. W. D. H.

**Phosphorus in Human and Cow's Milk.** By MAX A. SIEGFRIED (*Zeit. physiol. Chem.*, 1897, **22**, 575—578).—In cow's milk, the phosphorus of the nucleon accounts for only 6 per cent. of the total phosphorus; in human milk, where the nucleon is twice as abundant (see Wittmaack, preceding abstract), it accounts for 41·5 per cent. of the total phosphorus. The rest of the phosphorus in human milk is in the casein; there is practically no inorganic phosphorus.

W. D. H.

**Action of Acids and Alkalis on the Electrotonic Currents of Nerve.** By AUGUSTUS D. WALLER (*Proc. physiol. Soc.*, 1896—1897, 6—9).—The typical effect of acids is to augment the catelectrotonic and diminish the anelectrotonic current. Alkalis produce the opposite effect. W. D. H.

**Deep and Surface Temperature of the Body after Section of the Spinal Cord.** By MARCUS S. PEMBREY (*Proc. physiol. Soc.*, 1896—1897, 13—15).—The observations were made on a patient in whom the cord had been crushed. The surface temperature of the paralysed parts was high, even when the deep temperature was subnormal. The paralysed parts were dry compared with the non-paralysed portions of the body. W. D. H.

**Effect of a Meal on the Nitrogen of the Urine.** By OTTO VERAGUTT (*J. Physiol.*, 1897, **21**, 112—125).—After a meal rich in proteids, the output of nitrogen in the urine shows three rises, one immediately, the second 2 to 4 hours, and the third 6 to 7 hours later. If the food is poor in proteids, the three rises are still seen, but are not so well defined. The first rise is the most constant. Residence at 1000 metres above sea-level makes no difference in the result.

W. D. H.

**The Yellow Pigment of Urine.** By ARCHIBALD E. GARROD (*J. Physiol.*, 1897, **21**, 190—191).—Riva and Chiodera have stated that the action of potassium permanganate on urobilin is to convert it partially into a substance which has the characters of the yellow pigment of urine.

Conversely, in the present paper it is shown that the action of pure aldehyde on the yellow pigment (in neutral alcoholic solution) is to convert it very largely into a substance with the characters of urobilin.

The yellow pigment does not necessarily come, however, ultimately

from the bile pigment, but also, and perhaps primarily, from the blood pigment, urobilin being in each case an intermediate substance.

W. D. H.

**Albumosuria.** By KARL H. HUPPERT (*Zeit. physiol. Chem.*, 1897, **22**, 500—507).—Some years ago Noël-Paton (Abstr., 1893, ii, 290) described a crystalline proteid occurring in human urine. Crystallisation occurred spontaneously in the urine on standing, and the proteid was recrystallised after its separation from the urine by the use of ammonium sulphate. The present article points out that this proteid, which Noël-Paton considered to be a globulin, is probably heteroalbumose. The principal ground on which this conclusion is based is the concordance in its ultimate analysis with that of albumoses in other cases of albumosuria, and with that of Kühne's heteroalbumose.

W. D. H.

**Fibrinuria.** By DAVID M. GREIG (*J. Pathol. and Bacteriol.*, 1897, 4, 401—403).—The occurrence of urine which deposits a clot of fibrin on standing is a rare condition. The details of such a case are described; temporary congestion of the kidneys led apparently to an exudation of blood plasma, and this formed the source of the fibrin.

W. D. H.

**Multiple Intestinal Concretions in Man.** By CARL TH. MÖRNER (*Zeit. physiol. Chem.*, 1897, **22**, 522—525).—The concretions removed from the intestine of a man gave the following result on analysis:

| | | |
|---|---|---|
| Magnesium ammonium phosphate | 82·23 | per cent. |
| Calcium phosphate | 5·24 | ,, |
| Magnesium phosphate | 1·64 | ,, |
| Calcium carbonate | 1·61 | ,, |
| Calcium soap | 0·75 | ,, |
| Neutral fat | 0·20 | ,, |
| Insoluble organic substance | 1·90 | ,, |
| Water traces of soluble organic substances, &c. | 6·43 | ,, |

W. D. H.

**Chlorides and Phosphates of the Blood in Disease.** By WACLAW VON MORACZEWSKI (*Virchow's Archiv.*, 1896, **146**, 424—452).—The blood was investigated in a number of diseased conditions of diverse kinds. Clinical and chemical details are given in each case. In pneumonia, the chlorides are diminished; they rise after the crisis. The phosphates are abundant; this is usual in acute diseases, the urine showing a correspondence. In nephritis, there is an increase in the chlorides and a decrease in the phosphates. In lead poisoning, if lead is passing into the urine, the blood is rich in chlorides. The urine is poor in chlorides, rich in phosphates, the opposite to the blood; the same is true for anæmia. W. D. H.

**Physiological Action of Nitrites.** By JOHN S. HALDANE, R. H. MAKGILL, and A. E. MAVROGORDATO (*J. Physiol.*, 1897, **21**, 160—189).—A full account of experiments of which a preliminary notice has already appeared (this vol., ii, 63). W. D. H.

**Physiological Action of Choline, Neurine, and Allied Substances.** By FREDERICK WALKER MOTT, and WILLIAM D. HALLIBURTON (*Proc. physiol. Soc.*, 1896—1897, 18—20).—When injected into the circulation, small doses of choline hydrochloride cause a marked temporary fall of blood pressure, which is cardiac, and not peripheral in origin. It occurs also after section of the vagi. Neurine hydrochloride produces a preliminary fall and a subsequent rise of pressure, respiration being slowed and deepened. This drug is more toxic than choline, less than a decigram being the fatal dose in a dog; respiration ceases before the heart.

The physiological interest of these observations is derived from the fact that the cerebrospinal fluid, in cases of brain disease, where, as in general paralysis of the insane, there is great wasting of the brain substance and disintegration of its cells, produces exactly the same effects as solutions of choline. Normal cerebrospinal fluid is innocuous; the toxicity of the pathological fluid is due to some non-proteid substance precipitable by phosphotungstic acid. It is probable that this substance is choline, derived from the lecithin of the brain. If this is the case, the enfeebled circulation with severe fainting fits and fatty degeneration of the heart, so frequently seen in cases of general paralysis, will be in part accounted for. The blood removed by venesection from patients during the fits contains the same substance.

W. D. H.

**Physiological Action of Hydrastine Hydrochloride.** By CHARLES D. F. PHILLIPS and MARCUS S. PEMBREY (*Proc. physiol. Soc.*, 1896—1897, 4—6).—The effect of hydrastine hydrochloride on the various systems is described in detail; the most marked effect is convulsions similar to those produced by strychnine. The drug is used as an abortefacient, and the present experiments on cats confirm this; it, however, at the same time kills the offspring. W. D. H.

**Fermented Fish.** By CARL TH. MÖRNER (*Zeit. physiol. Chem.*, 1897, 22, 514—521).—In some parts of northern Sweden, fish are loosely packed in casks with a little salt, the casks are closed, and allowed to remain for some weeks. The fish, therefore, is eaten in what is practically a putrefied condition. The gases obtained were carbonic anhydride, hydrogen sulphide, and vapour of methyl mercaptan. Succinic acid is abundant, and so are both volatile, and solid fatty acids. Ammonia, methylamine, dimethylamine, trimethylamine, and choline were found among the bases. Leucine is present in abundance, and ethylic alcohol and acetone in small quantities. Tyrosine, indole, scatole, phenol, putrescin and cadaverine are absent.

W. D. H.

## Chemistry of Vegetable Physiology and Agriculture.

**Butylic Alcohol Fermentation.** By OSKAR EMMERLING (*Ber.*, 1897, 30, 451—453).—After repeated attempts to isolate Fitz's "*Bacillus butylicus*," a variety of hay, obtained from Alsace, was ultimately found to yield this organism.

The pure bacillus quickly sets up butylic alcohol fermentation in glycerol, producing from 100 grams of glycerol, 6·3 grams of pure normal butylic alcohol, and from 100 grams of mannitol, 10·5 grams of butylic alcohol. Comparison with Beyerinck's "*Granulobacter butylicum*" showed that the latter produced no trace of butylic alcohol from glycerol, although it gave it with grape sugar; it is not identical, therefore, with Fitz's bacillus.

On distilling the product of the action of the bacillus on grape-sugar, a small quantity of a solid substance melting at 60°, probably palmitic acid, passes over along with the ethylic alcohol and steam.

J. F. T.

**The Changes which take place in Milk, either Spontaneously or during Culinary Processes.** By ANTOINE BÉCHAMP (*Bull. Soc. Chim.*, 1896, [iii], 15, 426—455. See this vol., 113, 183).—A continuation of an historical review of the subject. M. W. T.

**Fermentation produced by Moulds.** By OSKAR EMMERLING (*Ber.*, 1897, 30, 454—455).—By the action of *Mucor racemosus* on 100 grams of cane-sugar in a solution containing 2 grams of potassium phosphate, 1 gram of magnesium sulphate, and 5 grams of potassium nitrate in 1500 grams of water, large quantities of carbonic anhydride are produced, together with 1·46 per cent. of ethylic alcohol and 0·31 gram of pure succinic acid, the latter being isolated by means of its lead salt. On extracting the filtrate from the lead salt with alcohol and evaporating, 1·83 gram of glycerol (identified by means of the acraldehyde reaction) were obtained.

The numbers representing the relative proportions of these substances produced in this fermentation are: alcohol 22, glycerol 1·85, and succinic acid 0·31. J. F. T.

**Hydrolysis of Melezitose by Soluble Ferments.** By EMILE E. BOURQUELOT and H. HÉRISSEY (*J. Pharm.*, 1896, [vi], 4, 385—387. Compare Abstr., 1896, ii, 322).—Distilled water which has been left in contact with a mature culture of *Aspergillus niger* for 3 days readily hydrolyses melezitose, most probably into *d*-glucose and touranose.

J. J. S.

**Action of the Oxidising Ferment of Mushrooms on Phenols and Phenolic Ethers.** By EMILE E. BOURQUELOT (*J. Pharm.*, 1896, [vi], 4, 241—248, and 440—447. Compare Abstr., 1896, ii, 383, and this vol., ii, 66).—The oxidising ferment is best obtained from *Russula delica*, or, in default of this, from *Lactarius velutinus*, Bert., or *L. vellereus*, Fr., but the latter yield less active solutions.

Phenol, in a slightly alkaline solution, is readily oxidised by the ferment. Quinol, pyrogallol, and its isomerides are also readily oxidised. Phloroglucinol, however, is oxidised but slowly. Anisoil and phenetoil, in aqueous alcohol, are readily oxidised; also guaiacol. The latter is not merely coloured by the oxidising ferment of mushrooms, but also by ferments from numerous phanerogams. The red colour produced on guaiacol can be changed to blue by adding $\alpha$-naphthol in aqueous alcohol. Acetylguaiacol and veratrole give yellowish-red precipitates; a solution of creosol first changes to green, and then becomes reddish-yellow, but, on shaking, it again turns green; finally, a yellowish

precipitate is formed. Acetyleugenol behaves in much the same way as eugenol. Vanillin, in 1 per cent. aqueous solution, gives a voluminous precipitate, and the reaction proceeds more readily in the presence of a little acid. Vanillic acid acts in much the same way.

J. J. S.

**Selection of Organic Nutritive Substances.** By WILHELM PFEFFER (*Bied Centr.*, 1896, **25**, 813—814; from *Pringheim's Jahrb.*, 1895, **28**, 205—268; and *Bot. Centr.*, 1896, **65**, 202).—In experiments with *Aspergillus niger* grown in a solution containing glycerol (1 per cent.) and dextrose (6 per cent.), it was found that the glycerol was not attacked, whilst with 2 per cent. dextrose and 7·3 per cent. glycerol, the dextrose was entirely consumed. *Penicillium* utilises glycerol in relatively large amounts. Lactic acid also is not attacked in presence of dextrose, whilst acetic acid is utilised in greater quantity than dextrose when they are present together. Small quantities of dextrose in presence of much peptone are entirely consumed. Both fungi attack dextro- and lævo-tartaric acids, but prefer the former. *Aspergillus flavescens*, and *Monilia candida* behave similarly, whilst *Aspergillus fumigatus*, *Mortierella reticulata*, *Saccharomyces ellipsoideus*, "rose yeast," "Levure de Duclaux," and *B. subtilis* utilise both acids equally.

Lævo-tartaric acid is an unsuitable food for such fungi as prefer the dextro-acid, but suitable for those which do not split up racemic acid.

As regards the relation between the nutritive value of organic substances and their chemical constitution, there is no definite rule; compounds very similarly constituted may have very different food values, and *vice versa*. The nutritive value also cannot be judged by the heats of combustion, which are, for example, identical in the case of the optical antipodes, which are frequently physiologically different.

The relative food value is generally estimated from the rate of development under equal conditions. The author also determined the amounts of dry fungus obtained by the consumption of 100 parts of nutritive matter. The relation is called the economic coefficient. In the case of *Aspergillus niger*, the following economic coefficients were obtained: glycerol = 20; dextrose = 43. With *Penicillium glaucum*, glycerol = 20; dextrose = 33.

*Aspergillus niger*, beer yeast, and *Saccharomyces ellipsoideus* in no case attacked mandelic acid. *Penicillium glaucum* behaved differently. Yeasts which split up racemic acid, seemed to prefer dextromandelic acid, whilst lævo-mandelic acid was chiefly consumed when inoculated with a mixture of putrefying bacteria.

N. H. J. M.

**Crystallisation of Xanthophyll (Carotin) and Proof of its Presence in Leaves.** By HANS MOLISCH (*Chem. Centr.*, 1896, i, 815—816; from *Ber. deut. bot. Ges.*, **14**, 18—28).—The author's 'potash' method of separating chlorophyll and xanthophyll in leaves is as follows. The fresh green leaves, either whole or in small pieces, are immersed in dilute alcohol containing 40 per cent. of alcohol by volume, and in which 20 per cent. by weight of potassium hydroxide is dissolved, and left in closed vessels in the dark until all the chlorophyll has been extracted. In many cases, one day suffices for the complete extraction of the chlorophyll, the whole of the xanthophyll

remaining in the leaves. After washing with water, the leaves are immersed in glycerol. Every cell which formerly contained chlorophyll is now seen under the microscope to contain crystals of xanthophyll; and whilst the epidermis and vascular bundles are free from these crystals, the assimilation parenchyma appears impregnated with them. In some few cases, the xanthophyll separates in yellow drops, or permeates the whole of the cell content. The crystals vary from yellowish to brownish orange, and exhibit a most remarkable nacreous lustre. Crystallographic examinations were made with the leaves of *Mimulus moschatus*, Dougl.; *Polygonum tinctorium*, L.; *Mercurialis annua*, L., and an etiolated leaf of wheat. The xanthophyll crystals obtained from *Viola odorata* have the form of very long, narrow tables. Their optical properties indicate that they belong to the rhombic system. Unmistakable differences in the crystals from various crystallisations render it improbable that they are all identical. They are soluble in ether, absolute alcohol, chloroform, carbon bisulphide, glacial acetic acid, and concentrated solution of chloral hydrate, but insoluble in dilute acids and alkalis, and in water and glycerol. With concentrated sulphuric acid or nitric acid, the crystals become indigo-blue, turning quickly yellow, however, in the latter case. Bromine water or vapour causes a fugitive blue coloration, and then the crystals become colourless.

With concentrated hydrochloric acid and phenol or thymol, the crystals, after a short time, become deep blue. In iodised chloral hydrate, they turn dirty green. All these reactions are best shown with leaves which have been freed as far as possible from water.

The author does not attempt to decide whether the crystals formed in this reaction are all xanthophyll or all carotin crystals, or whether these are identical or whether they consist in part of colouring matters nearly related to carotene. He names them all carotin, and understands by that term a group of closely-related colouring matters which are analogous to the colouring matter contained in the carrot. He has attempted to prove that the crystals are not coloured cholesterol crystals. E. W. W.

**Colouring Matters contained in Leaves, and the Relationship of Chlorophyll to the Colouring Matter of Blood.** By W. O. Alexander Tschirch (*Chem. Centr.*, 1896, i, 816—817; from *Schweiz. Woch. Pharm.*, **34**, 85—87).—The yellow-colouring matter of leaves and probably that also of flowers, is a mixture of xanthocarotin, whose solution shows three absorption bands in the violet, and xanthophyll, whose solution exhibits no bands, but absorbs the ultra violet rays (end-absorption). Both compounds were obtained in a crystalline form, and neither contains nitrogen. The chlorophyll of living leaves is probably the product of the union of two other compounds of which one is phyllocyanin, and the other a colourless compound of unknown composition. Phyllocyanin and its compounds exhibit absorption spectra, of which only two of the five bands seen in the visible part of the spectrum agree with those of the oxyhæmoglobin of blood. By employing a quartz spectroscope, the author has detected a new band at the end of the violet which agrees exactly with the principal absorption band of blood observed by Soret, resembling it also in its constancy

of position, which varies only between the lines G and M. The reddish yellow crystals of phyllopurpuric acid obtained from alkaline solutions of chlorophyll, that is, from salts of chlorophyllic acid, exhibit essentially the same spectrum, in the visible part of the spectrum, as the red hæmatoporphyrin prepared by Nencki from blood. The solutions of both show a red fluorescence.

Assuming that similarity of absorption spectra is indicative of similarity of atomic constitution, then chlorophyll must be nearly allied to the colouring matter of blood. Moreover, both series of compounds, on distillation with zinc, yield pyrroline, hence both evidently contain the pyrroline ring.

The quartz spectroscope employed by the author contained a quartz doublet lens in the collimator tube, and in place of the telescope a quartz lens. The prism was a Cornu prism composed of dextro- and lævorotatory quartz. The containing vessels were also of quartz, and the heliostat had a German-silver mirror. With this apparatus, the solar spectrum as far as the Fraunhofer line U could be photographed so that the additional portion of the spectrum was longer than the ordinary visible portion. Many phenomena hitherto named end-absorptions were found to consist of bands.

E. W. W.

**The Supply of Soil Nitrogen.** By EUGEN W. HILGARD (*Ann. Rep. Agric. Exper. Stat. Univ. California* for 1894—1895, 32—35).—Experiments were made to discover a plant suitable for the climate of California, for the purpose of green manuring, especially for orchards. It has been noticed that, when orchards have been carefully weeded for a number of years, their production decreases, notwithstanding the application of manures; the soil, moreover, deteriorates physically. A leguminous plant, *Tetragonolobus purpureus*, for which the name "square-pod pea" is proposed, seems likely to be suitable. It yields 24—26 tons per acre (equivalent to about 5 tons of hay). Its nitrogen percentage is less than that of lucerne or clover, but the nitrogen of the produce of an acre would be much greater. If sown in January, it could be ploughed in by the middle of May.

The alkali soils of California contain in the first 12 inches as much as 0·33 per cent. of soluble salts, consisting mainly of sodium chloride and sulphate, but containing no less than 12 per cent. of nitrate. This corresponds with 1400 lbs. of sodium nitrate per acre in the first 12 inches of soil.

N. H. J. M.

**Distribution of the Salts in Alkali Soils.** By EUGEN W. HILGARD and ROBERT H. LOUGHRIDGE (*Ann. Rep. Agric. Exper. Stat. Univ. California* for 1894—1895, 37—71).—Under ordinary circumstances, the alkali soils of California yield very heavy crops, or nothing at all, according to whether there is a heavy rainfall or not. With irrigation, good crops are certain for some years, after which, owing to evaporation and the consequent rise of alkali to the surface, the land becomes worse than before. The following numbers show the amounts of soluble salts (in lbs. per acre) in the soil and subsoil of unirrigated land, bearing natural vegetation.

| | Sodium. Nitrate. | Sodium. Chloride. | Sodium. Carbonate. | Alkali. Sulphates. | Total. |
|---|---|---|---|---|---|
| 1st 12 inches | 20 | 190 | 230 | 370 | 810 |
| 2nd ,, | — | 190 | 4140 | 730 | 4460 |
| 3rd ,, | — | 1040 | 13590 | 2450 | 17080 |
| 4th ,, | — | 20 | 4040 | 620 | 4680 |

The results are important as showing that the greater amount of the salts are not far from the surface, and that the amount is limited. The land can therefore be completely cured by underdrainage.

The application of gypsum (1·5 tons per acre) gives very good results with barley on land which was otherwise sterile. It was found that the percentage of sodium carbonate was greatly reduced at the surface, and even, though to a less extent, in the subsoil. The application of gypsum also had the effect of liberating potash from the zeolites of the soil, giving rise to an increase of potassium sulphate in the first 6 inches of soil. The nitrates were also increased.

In order to check evaporation, the land should be deeply tilled, and to enable the deep tilth to be maintained, crops should be grown which allow hoeing. This is, however, impossible in the case of "black" alkali soils; these must be treated with gypsum some time before sowing, after which irrigation may be necessary. N. H. J. M.

Growing Sugar Beets on Alkali Soils. By Eugen W. Hilgard and Robert H. Loughridge (*Ann. Rep. Agric. Exp. Stat. Univ. California* for 1894—1895, 71—91). Sugar beet of good quality can be grown on land containing as much as 12,000 lbs. of alkali salts per acre to the depth of 3 feet, provided that the amount of sodium chloride does not exceed 0·04 per cent. or 1,500 lbs. per acre. Carbonates are much less injurious than chlorides, and probably not more injurious to the quality of the roots than sulphates. The maximum amounts of carbonates and sulphates, when good roots were obtained, were respectively about 4,000 lbs. and 9,000 lbs. per acre in the first 3 or 4 feet of soil.

The appearance of a soil is not a sufficient guide, since compact soils show an efflorescence quite out of proportion to the small amount of alkali present, whilst loose soils, which show very little efflorescence, may contain excessive amounts of soluble salts. N. H. J. M.

Diminution of the Nitrogenous Matter in Wheat in the Department of Nord. By Balland (*Compt. rend.*, 1897, **124**, 158—159).—Eight samples of wheat grown in the Département du Nord, and analysed by Millon in 1848, contained from 10·23 to 13·02 per cent. of proteids in the normal condition, and 12·32 to 15·44 per cent. when dry. Six samples of wheat grown in the same locality in 1895, two in 1890, and one in 1887 were found by the author to contain from 8·96 to 10·62 per cent. of proteids in the normal state, and 10·36—12·51 per cent. when dry. Wheat now grown in Algeria contains the same percentage of proteids as the Algerian wheats examined by Millon. The yield per hectare in Algeria remains practically what it was in 1852, but that in the Département du Nord has been increased from about 14 hectolitres por hectare to 28 hectolitres. Schlœsing has shown that the proportion of proteids in wheat depends

on the richness of the soil in nitrogen, and the author suggests that a gradual exhaustion of the nitrogen in the soil explains the diminution observed in the wheat of the Département du Nord. C. H. B.

**Value of Creamery Separator Skim Milk for Pig Feeding.** By WILLIAM A. HENRY (*Ann. Rep. Agric. Exper. Stat. Univ. Wisconsin*, No. 12, for year ending June, 1895, 7—72).—A number of experiments are described in which pigs were fed with maize meal alone, and with maize meal together with different amounts of skim milk. The following average results show the weights (in lbs.) of meal and skim milk required to produce 100 lbs. gain in live weight.

| | Maize meal. | Skim milk. |
|---|---|---|
| Grain alone | 506 | — |
| Meal 1 lb. to skim milk 1—3 lbs. | 321 | 585 |
| ,, ,, ,, ,, 3—5 ,, | 265 | 1048 |
| ,, ,, ,, ,, 5—7 ,, | 250 | 1434 |
| ,, ,, ,, ,, 7—9 ,, | 207 | 1616 |

Taking the averages of all the experiments, it is seen that 462 lbs. of skim milk saved 100 lbs. of meal, the largest saving being when 1—3 lbs. of skim milk is used for each lb. of meal.

The chief value in the utilisation of skim milk is not, however, in saving meal, but in maintaining a healthy condition, and in promoting the rapid growth of the animals. N. H. J. M.

## Analytical Chemistry.

**Decomposition of Mercurous Chloride and the Estimation of free Chlorine.** By IYOTIBHUSHAN BHADURI, *Zeit. anorg. Chem.*, 1897, 13, 407—411).—When a neutral or alkaline solution containing chloride, chlorate, hypochlorite, and free chlorine is treated with an excess of mercury, the chloride and chlorate remain unaltered, the free chlorine forms mercurous chloride, and the hypochlorite forms mercuric oxide; further, the free chlorine acting on the hypochlorite forms hypochlorous acid, and this combines with mercury to form mercuric oxychloride, which is insoluble in water. The mixed precipitate of mercury compounds is separated by filtration, carefully washed, and then treated with a very slight excess of dilute hydrochloric acid. Mercurous chloride and free mercury remain undissolved. The quantity of mercuric chloride dissolved by the hydrochloric acid gives the quantity of hypochlorous acid, and the free chlorine is represented by the mercurous chloride. The chlorine in the latter compound is estimated by titration with alkali; but, in order to obtain correct results, it is necessary to boil the mixture for about 15 minutes, and, after allowing it to cool, to collect the residue, treat it again with alkali, collect and wash. The chlorine in the filtrates is estimated by means of silver nitrate, after acidification with nitric acid. E. C. R.

**Estimation of Oxygen in the Air and in Aqueous Solution.** By D. ALBERT KREIDER (*Zeit. anorg. Chem.*, 1897, 13, 418—426; also *Am. J. Sci.*, [iv], 2, 361—367).—The method consists in treating a

measured volume of air with strong hydriodic acid in the presence of nitric oxide, then neutralising the acid with potassium hydrogen carbonate and estimating the liberated iodine by means of N/10 arsenious acid. This method is similar to the one employed for the estimation of perchlorate previously described (Abstr., 1896, ii, 123); and the same precautions must be taken to exclude the air. 100 c.c. of air, calculated at 0° and 760 mm., is taken for each experiment, and the best quantity of nitric oxide to employ is 15 c.c. The results are accurate to 0·05 per cent.

It is proposed to estimate the oxygen dissolved in water in a similar manner; each experiment takes only about 10 minutes. The mean of the results gives 6·022 c.c. of oxygen in 1000 c.c. of distilled water at 20° and 760 mm.

A full description of the apparatus employed is given.

E. C. R.

**Estimation of Organic and Ammoniacal Nitrogen.** By Aimé Pagnoul (*Ann. Agron.*, 1896, **22**, 543—544).—The following modification of Kjeldahl's method is recommended. The substance (0·5—1 gram; or, if soil, 10 grams) is boiled with sulphuric acid (25 c.c.) and a drop of mercury; less than an hour is usually sufficient. The mixture is then poured into a flask with 200 c.c. of water, caustic soda solution (40 c.c.), is added, and the whole cooled. Zinc dust (about 1 gram), caustic soda (40 c.c.), and potassium sulphide (6 c.c.) are quickly added, and the distillation proceeded with. The condenser is a long tube which dips into acid of known strength; it is connected with the flask by means of a tin tube. To prevent the acid from getting too hot, the receiver is placed in a vessel containing cold water.

If the substance to be analysed contains nitrates, it is boiled for a short time with a few c.c. of ferrous chloride and hydrochloric acid before the sulphuric acid is added.

The caustic soda solution employed is prepared by heating soda-lime (1 kilo.) with distilled water (1 litre). The object of adding it in two separate portions to the acid is to avoid heating, and consequent possible loss of ammonia, before distilling. The sulphide solution contains potassium sulphide (200 grams), and caustic potash (100 grams per litre); of this solution, 6 c.c. suffices when 0·8 gram of mercury is employed.

N. H. J. M.

**Estimation of Nitrogen in Guano.** By E. Franke (*Chem. Zeit.*, 1896, **20**, 325—326).—Haselhoff has recommended that 5 grams of the guano should be extracted with water on a filter, the filtrate made up to 250 c.c., and the joint ammonia and nitric nitrogen estimated by Ulsch's process in 25 c.c. of the liquid (0·5 gram of the sample). The insoluble matter on the filter is then treated by Kjeldahl's method.

The author finds that the results obtained by this method are very seriously below the truth; this is, no doubt, due to the presence of nitrogenous organic matters soluble in water, but which are imperfectly decomposed by boiling with aqueous soda. The final conclusions are (1) that Jodlbaur's phenol sulphuric acid process works very well with samples of guano if they do not contain more than 2 per cent. of

nitre; (2) that the results are satisfactory if the guano is first treated in the manner directed by Ulsch (reduction with iron and sulphuric acid), and then at once by Kjeldahl's process. L. DE K.

**Analysis of Sodium Nitrate.** By AIMÉ PAGNOUL (*Ann. Agron.*, 1896, **22**, 541—543).—Analyses of sodium nitrate by Schlœsing's method are liable to an error of 1 per cent. or more. The indirect method in which the chlorine, sulphates, moisture, and insoluble matter are determined, and the nitrate estimated by difference, is a longer process but gives better results. Even an error of 10 per cent. in each determination (and in the same direction) will only give an error of less than 0·5 per cent. in the case of 96 per cent. sodium nitrate. Moreover, the exact nature of the impurity is ascertained by the indirect method.

In Schlœsing's method, a correction is necessary, especially when only small quantities of gas are obtained (as in water and soil analysis), as the gas is never completely absorbable by ferrous chloride. In order to make this correction, a graduated tube is employed, so constructed that a few c.c. of a mixture of ferrous chloride and hydrochloric acid can be admitted. After absorption, the residual gas is measured.

N. H. J. M.

**Sensitive Test for Nitrous Acid.** By E. RIEGLER (*Zeit. anal. Chem.*, 1896, **35**, 677—678).—To 5—6 c.c. of the liquid add 0·02—0·03 gram of crystallised 1 : 4-naphthylaminesulphonic acid, and shake well. Then add 2 or 3 drops of concentrated hydrochloric acid and shake again vigorously for a minute. Then pour upon the surface 20—30 drops of ammonia. At the surface of contact of the liquids, a rose colour will be developed, which is best observed by transmitted light.

M. J. S.

**Estimation of Citrate-soluble Phosphoric Acid by means of Molybdate Solution.** By MAX SCHMOEGER (*Chem. Zeit.*, 1896, **20**, 497—498).—Koenig has stated that citric acid, when present in excess, such as is the case when dealing with citrate-soluble phosphoric acid, entirely, or partially, prevents the precipitation of the phosphoric acid by means of molybdate solution. The author, on the other hand, finds that the phosphoric acid is completely precipitated.

If, to save trouble, magnesium mixture is added directly to the citric acid solution from basic slags, the phosphoric acid is also completely precipitated, but the precipitate is contaminated with silica; this may, however, be subsequently separated by means of hydrochloric acid in the usual way. L. DE K.

**Estimation of Citrate-Soluble Phosphoric Acid in Basic Slags by means of Citric Acid.** By MAX PASSON (*Zeit. angw. Chem.*, 1896, 677—678).—The author (Abstr., 1896, ii, 575) has modified his process so as to obtain a stronger solution which gives no trouble in the further stage of the manipulation. Ten grams of the sample is exhausted with half a litre of a 2·8 per cent. solution of citric acid for half an hour in a rotating apparatus; 75 c.c. of the filtrate is then boiled in a 300 c.c. flask with 20 c.c. of nitric acid, 15 c.c. of sulphuric acid, and a drop of mercury until the organic

matter has been destroyed, and, after adding 20 c.c. of a 10 per cent. brine, the liquid is made up to the mark, and 100 c.c. of the filtrate is treated by the molybdate or magnesia citrate process. L. DE K.

**Valuation of Borax.** By J. GEORGE HEID (*Zeit. angw. Chemie*, 1896, 679).—The following process is recommended. Ten grams of the sample is dissolved in water and made up to 250 c.c.; the chlorine in 125 c.c. of this solution is precipitated by means of nitric acid and silver nitrate, and after weighing the silver chloride, the corresponding amount of sodium chloride is calculated. 25 c.c. of the solution is mixed with excess of hydrochloric acid and evaporated to complete dryness on the water-bath, the residue dissolved in water, and the chlorine precipitated as before. The difference between the two results gives the amount of sodium chloride corresponding with the borax present. If, to save time, a volumetric estimation of the chlorine is preferred, the dry mass, before dissolving it in water, must be repeatedly extracted with absolute alcohol to remove the boric acid. L. DE K.

**Organic Analysis by Analysis of the Gases produced in the Berthelot Calorimetric Bomb.** By NATHAN ZUNTZ and JOH. FRENTZEL (*Ber.*, 1897, **30**, 380—382).—The authors propose to carry out an organic analysis at the same time as a determination of the heat of combustion, especially with samples of food-stuffs, manures, &c. For this purpose, the bomb is weighed after the introduction of the oxygen, of which the composition is found by careful analyses. At the close of the combustion, samples of the gas contained in the bomb are analysed, and the total weight of the gas is found by deducting the weight of the water and nitric or other acid which is formed, together with the ash of the substance, from the sum of the weights of the gas put into the bomb, and of the substance taken. The results as regards carbon and hydrogen are satisfactory, whilst as regards nitrogen they are less so. No analyses are quoted.

A. H.

**Estimation of Potassium.** By ALBERT PRAGER (*Chem. Zeit.*, 1896, **20**, 269. Compare this vol., ii, 160).—The author states that when potassium chloride in dilute solution is slowly evaporated with platinic chloride, the platinochloride formed is more crystalline and purer than the product obtained in the usual way.

The following process is recommended for the analysis of compounds containing the potassium as sulphate. The solution is carefully precipitated with barium chloride, excess being avoided, and the filtrate is diluted to 75 c.c.; after adding the solution of platinic chloride, the mixture is evaporated on the water-bath, which should not boil, until the surface becomes covered with crystals; it is then allowed to cool, and when cold the evaporation is again continued until about 5 c.c. of liquid is left. When cold, 20 c.c. of 96 per cent. alcohol is added, and the precipitate washed, on a weighed filter with 80 per cent. alcohol and finally dried at 110°. As some kinds of filter paper contain matters soluble in alcohol and water, the author advises washing the filter before weighing, first with alcohol and then with hot water, drying finally at 110°. L. DE K.

**Estimation of Potassium.** By FREDERICK T. B. DUPRÉ (*Chem. Zeit.*, 1896, 20, 305).—Ruer (this vol., ii, 160) has proposed to calculate the amount of potassium chloride from the platinochloride by multiplying by 0·304 instead of 0·3056, the factor proposed by Fresenius. The author states that the latter is absolutely correct if Fresenius's instructions are carefully followed, but it is not possible to get potassium platinochloride in such a state of purity that it absolutely corresponds with the formula; different methods of analysis, therefore, require different factors. L. DE K.

**Estimation of Lime in Raw Materials used for Cement-making.** By FRITZ KLUGE (*Chem. Zeit.*, 1896, 20, 372).—Two grams of the finely-powdered sample, after being heated in a platinum crucible, over the blow-pipe, for about 10 minutes, is weighed, removed from the crucible and boiled with 50 c.c. of water; 40 c.c. of standard sulphuric acid is next added, and the excess of acid titrated with standard potash using phenolphthalein as indicator.

The acid and alkali should have been checked by means of a limestone of known composition similar in quality to the stone under examination. The results are very satisfactory, and the analysis can be finished in about 20 minutes. L. DE K.

**Separation of Thorium from the other Rare Earths by Potassium Nitride.** By LOUIS M. DENNIS (*Zeit. anorg. Chem.*, 1897, 13, 412—417).—A solution of potassium nitride is prepared by neutralising a dilute solution of azoimide with pure potassium hydroxide and then adding an excess of azoimide. When a solution of thorium chloride or nitrate is treated with the above solution and boiled for one minute, the thorium is quantitatively precipitated as thorium hydroxide. (Abstr., 1894, ii, 256). From a mixture of the rare earths prepared from Brazilian monazite, the thorium is also completely precipitated in a pure state, and the purity of the precipitate is independent of the relative amounts of thorium and the other rare earths.

E. C. R.

**Separation of Aluminium from Iron.** By FRANK A. GOOCH and F. S. HAVENS (*Zeit. anorg. Chem.*, 1897, 13, 435—440; also *Amer. J. Sci.*, 1896, [iv], 2, 416—420).—The method is based on the insolubility of aluminium chloride in a mixture of ether and hydrochloric acid, whereas ferric chloride is easily soluble.

A measured quantity of aluminium chloride solution (0·0761 gram $Al_2O_3$) was evaporated to dryness in a platinum dish, a solution of ferric chloride (0·15 gram $Fe_2O_3$) added; then 15 c.c. of a mixture of equal parts of strong hydrochloric acid and ether, and the mixture saturated with hydrogen chloride at 15°; a further 5 c.c. of ether was added, and the mixture again saturated with hydrogen chloride. The precipitated aluminium chloride was collected on asbestos in a filter-crucible, washed with a mixture of ether and hydrochloric acid, saturated with hydrogen chloride, and dried for half an hour at 150°; it was then heated with 1 gram of mercuric oxide, at first gently and finally over the blow-pipe, and weighed as $Al_2O_3$. The results were accurate. Instead of heating with mercuric oxide, the aluminium chloride may be redissolved and precipitated with

ammonia. Care must be taken that sufficient ether is present in the mixture, as otherwise the solution separates into two layers, the lower one consisting of a green, oily layer of ferric chloride dissolved in ether.

E. C. R.

**Estimation of Sesquioxides in Phosphates and Superphosphates.** By VON GRUEBER (*Zeit. angw. Chem.*, 1896, 741—742).—Ten grams of the sample is heated in a porcelain dish with 150 c.c. of water and 20 c.c. of hydrochloric acid, the whole evaporated to dryness, and the residue treated with dilute hydrochloric acid, filtered, if necessary, and made up to 500 c.c.

Fifty c.c. of the solution is heated in a 200 c.c. flask and nearly neutralised with 20 per cent. aqueous soda; 30 c.c. more of the soda solution is then added, and the whole boiled for ten minutes. When cold, the liquid is made up to the mark, filtered, and 100 c.c. of the filtrate slightly supersaturated with hydrochloric acid; the alumina is then precipitated as phosphate by adding a slight excess of ammonia, and boiling for a short time. The weight of the phosphate multiplied by 41·8 gives the amount of alumina in 0·5 gram of the sample.

One hundred c.c. of the solution is placed in a 250 c.c. flask, and the iron is reduced by means of metallic zinc and then estimated by means of potassium permanganate according to Fresenius's directions.

L. DE K.

**Estimation of Manganese in Spiegels, &c.** By H. BREARLEY (*Chem. News*, 1897, 75, 13—16).—The author, after searching investigation, adopts the following method. One to 1·5 gram of 20 per cent. spiegeleisen or a proportionate amount of other manganiferous iron is dissolved in hydrochloric acid, oxidised with nitric acid, filtered, if necessary, through a small asbestos filter, neutralised with sodium carbonate, diluted to about 900 c.c. and treated with a 3·75 per cent. solution of sodium acetate at the rate of 20 c.c. per gram of iron. It is then boiled and measured, noting the temperature; enveloped in cloth to retard cooling, and half the volume syphoned or filtered off, again noting the temperature. The liquid is cooled, neutralised with sodium carbonate, acidified slightly with acetic or sulphuric acid, then run into sufficient 0·3156 per cent. potassium permanganate solution containing 10 c.c. of 20 per cent. zinc sulphate solution, shaking constantly, allowed to settle, an aliquot part filtered off, acidified, and determined with ferrous ammonium sulphate and permanganate. Corrections being made for the variations in volume due to temperature, the calculations are as usual.

D. A. L.

**Colorimetric Estimation of Iron by Means of Potassium Thiocyanate.** By ARTHUR BORNTRAEGER (*Chem. Zeit.*, 1896, 20, 398—399).—The author compares the intensity of the red colour produced on adding potassium thiocyanate to the solution under examination with that obtained with an iron solution of known strength.

The method is more particularly intended for the estimation of traces of iron in the ash of wines or beers. The other salts contained in the ash do not influence the accuracy of the process.

L. DE K.

**Estimation of Tin and Copper in Tin-dross.** By L. Rürup (*Chem. Zeit.*, 1896, **20**, 406).—In analysing the dross formed in tin-baths for tinning iron, copper, &c., 500 grams of the well mixed sample is fused in a Hessian crucible with cream of tartar, sodium carbonate and chalk for about half an hour. The crucible, rapidly cooled, is broken, and the metallic button cleaned and weighed. About 1 gram of borings obtained from this is analysed by digesting it with 22 c.c. of nitric acid, sp. gr. 1·2, adding 10 c.c. of the concentrated acid, collecting the stannic acid produced, and converting it into stannic oxide by ignition. The filtrate is evaporated to dryness, and after dissolving the residue in dilute sulphuric acid, the copper is precipitated electrolytically. L. de K.

**Use of Organic Acids for the Estimation of Vanadium.** By Philip E. Browning and Richard J. Goodman (*Zeit. anorg. Chem.*, 1897, **13**, 427—434; also *Amer. J. Sci.*, [iv], **2**, 355—360).—The authors have examined the applicability to the estimation of vanadium of the method described by Browning (Abstr., 1894, 483) which consists in reducing vanadic acid to vanadium tetroxide by boiling with tartaric acid, and then titrating with iodine. When estimating vanadium by this method in the presence of molybdenum and tungsten, the presence of sodium tungstate does not affect the results; ammonium molybdate is, however, strongly reduced by boiling with tartaric acid. Trustworthy results can, however, be obtained if the reduction is allowed to take place at the ordinary temperature, leaving the mixture for one day. Oxalic and citric acids can be employed in place of tartaric acid, but the mixture must then be boiled. With citric acid, however, the oxidation by iodine proceeds more slowly, and one hour is necessary to complete the reaction, whereas with oxalic acid, it is complete in a quarter of an hour, and with tartaric acid in 30—40 minutes. A large excess of oxalic or tartaric acid does not influence the result, but an excess of citric acid must not be employed or the results will be too high.

For each tenth of a gram of vanadic acid present in the mixture, 1 gram of the organic acid is employed. After reduction, the cold solution is mixed with potassium hydrogen carbonate in the proportion of 5 grams for each gram of organic acid employed, and then a slight excess of iodine is added. The excess of iodine is destroyed by arsenious acid, and the mixture titrated with iodine in the presence of starch.

E. C. R.

**Estimation of Nitrites in Waters.** By Barbet and Jandrier (*J. Pharm.*, 1896, [vi], **4**, 248—249).—The authors propose resorcinol as a substitute for metaphenylenediamine in the estimation of nitrites in water. 0·1 gram of resorcinol is dissolved in 2 c.c. of the given water, and 1 c.c. of pure concentrated sulphuric acid is added in such a way that it forms a clear layer below the aqueous solution. At the junction of the two liquids a coloration is developed, which becomes deeper after gentle shaking. At the end of an hour, the tint obtained is compared with that resulting from solutions containing known quantities of nitrite. Waters containing even $\frac{1}{10000000}$ part of nitrite give a characteristic rose coloration. J. J. S.

**Apparatus for Estimating small Quantities of Marsh-Gas and other Gases in the Air of Coal-Mines.** By RUDOLF JELLER (*Zeit. angw. Chem.*, 1896, 692—702).—A somewhat complicated apparatus made on the Hempel principle, but filled with water instead of mercury. The difference in pressure is noted before and after treating the gas with absorbents, or submitting it to combustion.

L. DE K.

**Estimation of Invert-Sugar.** By A. LEYS (*J. Pharm.*, 1896, [vi], 4, 488—490).—In the volumetric estimation of glucose and also of invert-sugar, the author finds that the final point can be observed much more readily if the saccharine solution is alkaline and not acid. It is therefore advisable, after the inversion of cane-sugar by means of hydrochloric acid, to neutralise it, or render it alkaline, with potash before titrating with Fehling's solution. J. J. S.

**Conditions Affecting the Volumetric Estimation of Starch by means of a Solution of Iodine.** By FANNIE T. LITTLETON (*Amer. Chem. J.*, 1897, 19, 44—49).—The author finds that, for equal weights of starch, the depth of colour produced varies with the size of the granules; moreover, the intensity of the colour produced with different quantities of starch is not proportional to the amount of starch present, and is also greatly influenced by the presence of proteid matter. The method can only be used with substances containing a large amount of starch, and the solutions to be compared should be as nearly as possible identical.

Chloroform extracts iodine from starch iodide solution, even in presence of a large excess of starch. A. H.

**Different Methods for Estimating Cellulose.** By H. SURINGAR and BERNHARD TOLLENS (*Zeit. angw. Chem.*, 1896, 712—719; 742—750).—The authors have made a thorough investigation of the various processes in use for the estimation of cellulose, and have tabulated the results.

Lange's process, fusing with potassium hydroxide, yields a fairly pure cellulose, but causes a considerable loss, whilst Gabriel's method of treating with glycerol and potassium hydroxide yields an impure product. The chlorine method of Cross and Bevan is only to be recommended as a conventional process for testing jute. The best process seems to be the chlorate method recommended by Schulze, but the authors have not yet made a sufficient number of experiments to be able to speak decisively. L. DE K.

**Estimation of Aldehyde in Alcohol.** By JOSEF PAUL (*Zeit. anal. Chem.*, 1896, 35, 647—659).—The method is a colorimetric one in which the reaction with a solution of magenta decolorised by sulphurous acid is employed, but the conditions are defined with greater precision than heretofore. To prepare the reagent, the purest 'diamond' magenta is dissolved in 1000 parts of cold water and the solution filtered; a volume which contains 0·05 gram of magenta is then mixed with an aqueous solution of sulphurous acid containing (by iodine titration) exactly 0·5 gram of $H_2SO_3$, and the mixture is made up to 100 c.c. In well-stoppered bottles, the reagent can be kept for

several days. The aldehyde-free alcohol required can only be obtained by boiling a large quantity (8 litres) of alcohol in a flask with an inverted condenser fed with water of 50—60°; and removing the uncondensed aldehyde vapour by inserting into the condenser a tube connected with an aspirator. After several days, the alcohol may be slowly distilled over, but the first 3 litres and the last litre must be rejected. Any form of colorimeter may be used, but those of Krüss and Duboscq are recommended as convenient. All specimens of alcohol are diluted to 30 vols. per cent. unless the amount of aldehyde present is too small to admit of such dilution. A few "type solutions" are prepared, containing 25, 50, and 100 milligrams of aldehyde per litre of (30 vols.) alcohol, and since the intensity of the colour is only proportional to the amount of aldehyde within narrow limits, it is necessary so to dilute (with pure 30 vol. alcohol) the specimen of alcohol under examination that it may contain approximately the same proportion of aldehyde as one of these type solutions before finally measuring in the colorimeter the lengths of solution which give the same depth of colour. The operation is thus performed. Equal volumes of the type solution and the alcohol to be assayed are brought to 16° by immersing them in the same vessel of water; equal volumes of the reagent are then added simultaneously, and after 25 minutes the mixtures are transferred to the colorimeter and a series of readings made as rapidly as possible. For the 25 milligram and weaker types, 1 vol. of reagent is added to 10 vols. of alcohol; for stronger types, the amount of reagent is proportionally increased. Should the observed lengths differ by more than $\frac{1}{10}$th, a fresh adjustment of aldehyde concentration is necessary, and if the adjustment of aldehyde is carried on until equal columns give equal depths of colour, the observations may be made in a pair of ordinary test-tubes of equal diameter in front of a sheet of white paper.

Acetal in alcohol may be estimated in the same way. The acetal is hydrolysed by the sulphurous acid according to the equation $C_2H_4(OC_2H_5)_2 + H_2O = C_2H_4O + 2C_2H_5 \cdot OH$, so that the acetal is calculated from the aldehyde found.

Equally good results were obtained by the use of methylviolet 5 R from the Elberfeld factory in place of magenta. M. J. S.

**Action of Stannous Chloride on Ethereal Oils.** By EDUARD HIRSCHSOHN (*Chem. Centr.*, 1896, i, 755; from *Pharm. Zeits. Russ.*, 35, 65—69).—The author has found that Gurjun balsam oil and stannous chloride (Abstr., 1896, ii, 508) give a red coloration which turns violet and then blue. The behaviour of a large number of very various ethereal oils towards this reagent has now been further investigated by him; of these, only those of patchouli, musk, and valerian give a reaction similar to that of Gurjun balsam oil. The oils of celery seed, cubebs, galangal, laurel, sandal wood (some kinds), pepper, and cardamoms give a red to a pale rose colour. Wormwood and camomile oils furnish a green to bluish-green coloration. E. W. W.

# General and Physical Chemistry.

**Relation between the Refraction of the Elements and their Chemical Equivalents.** By JOHN H. GLADSTONE (*Proc. Roy. Soc.*, 1896, **60**, 140—146).—A list of the specific refractions $(\mu-1)/d$ and the atomic refractions $P(\mu-1)/d$ of the elements is given, as deduced from observations of the element itself, its salts or other compounds. In a paper by the author on the refraction equivalents of the elements (*Phil. Trans.*, 1870), it was shown that if the metallic elements be arranged in the order of their specific refractions, they are roughly in the inverse order of their combining proportions. It was subsequently shown that the specific refractive energy of a metal is inversely as the square root of its combining proportion. The data collected in the present paper serve to test this generalisation throughout the whole range of the metallic elements. If $S$ is the specific refraction and $E$ the chemical equivalent of the metal, then $SE^{\frac{1}{2}}$ should have a constant value. For this product, the author proposes the name "refractive constant of equivalent weights." A review of the tables given shows that metals which have the same valency have the same or nearly the same constant of refraction for equivalent weights. The constants of the bivalent, trivalent, quadrivalent and apparently quinquivalent groups are practically the same, ranging about 1·01. When a metal combines in a proportion that indicates a lower valency than that ordinarily assigned to it, its constant is somewhat elevated.

If the constants are calculated for the square root of the atomic weight instead of that of the combining proportion, the following mean values are obtained:

| | | |
|---|---|---|
| Univalents...1·30 | Trivalents.........1·75 | Quinquivalents...2·19 |
| Bivalents ...1·40 | Quadrivalents ...2·12 | |

The fact that these numbers increase nearly in the proportion of the square roots of 2, 3, 4 and 5, indicates that the relation involved is not between the specific refraction and the atom, but rather between it and the combining proportion or chemical equivalent of the metal. This brings the optical property into analogy with Faraday's law of electro-chemical equivalents. H. C.

**Influence of Temperature on Rotatory Power.** By PHILIPPE A. GUYE and EMILY ASTON (*Compt. rend.*, 1897, **124**, 194—197). The authors have determined the specific rotatory powers between 15° and 100° (approximately) of valeric acid, secondary amylic alcohol, amylic benzoate, secondary amylic chloride, amylic paratoluate, propylglycol chlorobromhydrin, secondary amylic chloracetin, propylglycol chlorochloracetin, propylglycol chlorobutyrin, primary amylic alcohol, propylglycol chloracetin, propylic $\beta$-methyladipate, ethylic $\beta$-methyladipate, amylic chloracetate, methylic chlorosuccinate, ethylic chloromalate, methylic phenylglycollate, and ethylic phenylchloracetate. In all cases, the rotatory power diminishes as the temperature rises, the phenomenon being continuous throughout the interval specified. There are now at

least fifty optically active liquids the rotatory powers of which are known to diminish with a rise of temperature. C. H. B.

**Rotatory Power and Structure.** By PHILIPPE A. GUYE and J. GUERCHGORINE (*Compt. rend.*, 1897, **124**, 230—233).—The following specific gravities and specific rotatory powers have been determined, and the molecular refractions calculated by the $n_2$ formula.

| | Sp. Gr. between 15° & 20°. | Mol. Refraction. (Obs.) | $[\alpha]_D$. |
|---|---|---|---|
| Amylic valerate | 0·8629 | 49·69 | +2·99 |
| Amylic isovalerate | 0·8553 | 50·05 | +2·69 |
| Amylic valerate (racemic) | 0·8607 | 50·58 | +3·02 |
| Propylic valerate | 0·8653 | 40·80 | +1·99 |
| Isopropylic valerate | 0·8510 | 40·90 | +2·54 |
| Butylic valerate | 0·8643 | 45·31 | +1·86 |
| Isobutylic valerate | 0·8565 | 45·30 | +1·41 |
| Secondary butylic valerate | 0·8534 | 45·48 | +2·12 |
| Racemic amylic valerate | 0·8548 | 50·40 | +1·42 |
| Propylic caproate | 0·8688 | 49·99 | +1·87 |
| Isopropylic caproate | 0·8650 | 49·88 | +2·10 |
| Butylic caproate | 0·8668 | 54·49 | +1·61 |
| Isobutylic caproate | 0·8653 | 54·36 | +1·28 |
| Secondary butylic caproate | 0·8656 | 54·10 | +1·88 |

There are three series of isomeric propylic compounds and three series of isomeric butylic compounds amongst the ethereal salts derived from active amylic alcohol. If the gradual decrease in rotatory power in each of these series is taken into account, it follows that in all the series the propyl group behaves as if it were heavier than the isopropyl group, whilst the isobutyl group behaves as if it were heavier than the normal butyl group, and this in its turn as if it were heavier than the secondary butyl group. C. H. B.

**Spectra of Metalloids in Fused Salts: Silicon.** By ARNAUD DE GRAMONT (*Compt. rend.*, 1897, **124**, 192—194).—When a highly condensed spark is allowed to impinge on silicates fused on a platinum spatula (compare Abstr., 1896, ii, 585), the spectrum of the spark shows the following lines of silicon: 6969·7 strong, 6342·2 very strong, 5978·9 somewhat strong; 5960·3 distinct, 5948·0 doubtful, 5060·0 and 5045·5 very strong; 4575·7 very feeble, 4568·9 somewhat distinct, 4553·7 distinct, 4131·3 and 4129·2 somewhat strong, but diffuse. The wave-lengths are the means of determinations with the spark and the fused salts, and with a spark between silicon poles in very pure hydrogen. The most characteristic lines are 6969·7 and 6342·2 in the red, and 5060·0 and 5045·5 in the green. The latter are much more intense than the adjacent lines of platinum and air.

The spectrum is well shown by sodium silicate, and not quite so well by the potassium salt, particularly well by potassium or sodium silicofluoride, but not at all well by zinc silicate. Natural silicates, very finely powdered and fused with sodium carbonate, soon show the pairs of lines in the red and the green respectively. C. H. B.

**Theory of Lead Accumulators.** By C. LIEBENOFF (*Chem. Centr.*, 1896, i, 349; from *Zeit. Electrotechn. und Electrochem.*, 1896, 2, 420—422).—According to the author's view, in secondary cells the sulphuric acid acts as the electrolyte, lead sulphate being too insoluble and water not readily dissociated. When the charging current passes into the accumulator, the ions $\overset{--}{PbO_2}$ and $\overset{++}{Pb}$ separate out, and are replaced in the solution at the expense of the lead sulphate of the plates; only when the latter has been thus fully converted into spongy lead and peroxide will separation of the ions $\overset{-}{OH}$ and $\overset{+}{H}$ take place. During discharge, the reverse reactions take place. H. C.

**Theory of Lead Accumulators.** By WALTHER LOEB (*Chem. Centr.*, 1896, i, 785; from *Zeit. Electrotechn. und Electrochem.*, 1896, 2, 495).—The author's views with reference to the reactions taking place in lead accumulators are similar to those of Liebenoff (see preceding abstract), the dissociation of the water present into H and OH ions being, however, regarded as a primary action, and essential for the production of the $PbO_2$ ion. H. C.

**Electrical Resistivity of Pure Mercury at the Temperature of Liquid Air.** By JAMES DEWAR and JOHN A. FLEMING (*Proc. Roy. Soc.*, 1896, 60, 76—81).—The electrical resistivity of carefully purified mercury was measured between the temperature of liquid air and $+35°$, the results being given in the paper in tabular and curve form. The resistivity decreases gradually from $+35°$ to the temperature $-36°$ on the platinum scale. At this point, the resistivity rapidly decreases to about one-quarter of its value in falling from $-36°$ to $-50°$, and this sudden change all takes place within the range of about 14° of tempera ture. At the temperature of $-50°$ on the platinum scale, the resistivity again changes direction, and continues downwards, in such a direction as to show that if produced along the same line from the lowest temperature actually observed, $-204°$ on the platinum scale, it would pass exactly through the absolute zero of temperature on this scale. The part of the curve which corresponds with the mercury in the liquid state is almost exactly parallel to that part of the curve which corresponds with mercury in the solid condition, although, owing to the difference in the absolute values of the resistivities at these parts, the temperature coefficients, as usually defined, are very different. In the solid condition, between the temperatures of $-197·9°$ and $-97°$, the mean increase in resistivity is 93·14 C. G. S. units per degree rise of temperature on the platinum scale; between $-108·4°$ and $-57·6°$ the mean increase in resistivity in C. G. S. units per degree is 109·6; in the liquid condition between the temperature $-35·2°$ and 0° the mean increase per degree is 83·2 C. G. S. units. Temperatures defined by the platinum scale do not differ by more than 0·5° from the centigrade scale down to $-100°$, but the temperature of boiling liquid oxygen, which on the centigrade scale is denoted by $-182°$, is on the platinum scale denoted by $-196·7°$. The temperature coefficient as usually defined is therefore 0·000884 between $-35°$ and 0°.

The measurements afford a further confirmation of the law that the

electrical resistivity of a pure metal vanishes at the absolute zero of temperature. H. C.

**Electrical Resistivity of Bismuth at the Temperature of Liquid Air.** By JAMES DEWAR and JOHN A. FLEMING (*Proc. Roy. Soc.*, 1896, 60, 72—75).—The anomalous results obtained by the authors (Abstr., 1896, ii, 5) for the resistivity of certain samples of bismuth at various temperatures down to that at which air solidifies, have led them to repeat the determinations with specially prepared pure electrolytic bismuth. The values obtained show that, in the case of pure electrolytic bismuth, there is no tendency of the resistivity curve to a minimum value. Down to the lowest temperatures reached, the resistivity continues to decrease in a perfectly regular manner, and in such a way as to show that it would be no exception, in all probability, to the ordinary law, that resistivity of pure metals vanishes at the absolute zero of temperature. With this electrolytic bismuth, the observation was confirmed that the effect of a given transverse magnetic field in increasing the resistivity of bismuth is immensely increased by cooling the bismuth to the temperature of liquid air. The effect of cooling with liquid air can be more than nullified by the field, and pressed to its limit it would appear that pure bismuth, which would in all probability be made a perfect conductor by reducing to the absolute zero of temperature, would be then converted into a non-conductor, if at the same time immersed in a magnetic field of sufficient strength. H. C.

**Dielectric Constants at Low Temperatures.** By RICHARD ABEGG (*Ann. Phys. Chem.*, 1897, [ii], 60, 54—60).—Making use of the method devised by Nernst (Abstr., 1894, ii, 437), the author has determined the dielectric constants for toluene, ether, acetone, amylic and ethylic alcohols, and also for a solution of 1 vol. of water in 10 vols. of ethylic alcohol, between the temperatures $+19°$ and $-87°$. The dielectric constants in all cases increase rapidly as the temperature falls, the temperature coefficient being greater the greater the value of the constant. As there is an almost constant proportion between the dielectric constant and its temperature coefficient in all cases, a formula of the type $-dD/dT = D/190$ may be taken to express the results. This gives on integration $D = ce^{-\frac{T}{190}}$, a formula which is found to be in close accordance with the experimental results. H. C.

**Electromotive Force and Partition Equilibrium.** By ROBERT LUTHER (*Zeit. physikal. Chem.*, 1897, 22, 85—92).—The author replies to Bucherer's claim for priority (Abstr., 1896, ii, 461 and 586), and states that, although the results of the latter were in print earlier than his own, yet his were read as a dissertation thesis at an earlier date. The conclusions of Bucherer are not purely thermodynamical deductions, but rest on various assumptions, as, for example, the greater solubility of electrolytes in water than in aqueous alcohol. L. M. J.

**Molecular Conductivity of Rubidium and Cæsium Chlorides.** By BERTRAM B. BOLTWOOD (*Zeit. physikal. Chem.*, 1897, 22, 132—133). —According to Bredig (Abstr., 1894, ii, 226), the ion velocities of rubi-

dium and cæsium, obtained by measurement of the conductivity of the chlorides, are respectively 73·5 and 73·6 at 25°. Baur, however, obtained the values 76·5 and 79·3 from the same salts (Abstr., 1896, ii, 144). The numbers being of interest from the periodic law standpoint, the conductivities were redetermined at concentrations $v =$ 32, 64, 128, 256, 512, and 1024, giving, after correction for the conductivity of the water, the value $\mu_\infty(RbCl) = 144·5$ and $\mu_\infty(CsCl) = 144·8$, which lead to the velocities $Rb = 74·3$ and $Cs = 74·6$.

L. M. J.

**Electrolytic Solution and Separation of Carbon.** By Alfred Coehn (*Chem. Centr.*, 1896, i, 985, from *Zeit. Electrotechn. und Electrochem.*, 1896, 2, 541).—Bartoli and Papasogli noticed that, during the electrolysis of dilute sulphuric acid with carbon electrodes, carbonic oxide and carbonic anhydride make their appearance along with oxygen at the anode. By suitable alteration in the concentration of the acid, the temperature, and the current density, the author succeeded in carrying out the electrolysis in such a manner that carbonic oxide and carbonic anhydride were almost alone produced at the anode. The gaseous mixture contained 70 per cent. $CO_2$, about 30 per cent. CO, and 1 per cent. $O_2$. At low temperatures, a distintegration of the anode takes place, and suspended particles of carbon find their way into the acid. At high temperatures, carbon dissolves in the acid, the solution being coloured from yellow to a reddish-brown. If the solution thus formed is electrolysed, using a platinum cathode, a deposit of carbon is obtained, at first as a thin, coloured film and then as a graphitic deposit. The solution reduces Fehling's solution and probably contains carbohydrates. In reversal of the above process, a cell was formed by means of a lead peroxide plate and a carbon electrode, in which, working under the conditions previously maintained, the carbon acts as the soluble electrode. This gave 1·03 volt. with an external resistance of 100 ohms and yielded a constant current until the lead peroxide plate was exhausted.

H. C.

**Electrolysis of Copper Sulphate Solutions.** By Fritz Foerster and O. Seidel (*Zeit. anorg. Chem.*, 1897, 14, 106—140).—The authors' experiments prove that the electric current is capable of converting the bivalent copper ions at the cathode in copper sulphate solutions into univalent ions, whereby cuprous sulphate is formed. The latter is tolerably stable in the presence of copper sulphate in acid solution under certain conditions, but in a neutral solution, hydrolysis takes place with the separation of cuprous oxide.

The electrolysis of copper sulphate solutions containing from 4 to 0·05 equivalents per litre, either neutral or mixed, with 0·01 to 1 equivalent of sulphuric acid, and heated at 100°, was examined. The electrolyte was stirred, and protected from air by a current of pure hydrogen. From neutral and very slightly acid solutions, less cuprous oxide, and from stronger acid solutions less copper, than the quantity corresponding with the current employed is deposited. In a solution containing 2 equivalents of copper sulphate and 0·1 or 1·0 equivalent of sulphuric acid, however, with a current density of 0·135 ampères per 100 square centimetres, hardly anything is deposited at the

cathode; from this, the authors conclude that the current has effected the conversion of copper sulphate into cuprous sulphate, which, under these conditions, is stable. The stability is determined by the number of cupric ions present, and generally increases with the concentration of the copper sulphate. In neutral solution, cuprous oxide is deposited, but a N/10 solution of sulphuric acid is sufficient in a 2N solution of copper sulphate to prevent the hydrolysis to a great extent; as the solution cools, sparkling crystals of pure copper are deposited. The same crystalline deposit of copper is obtained by dissolving cuprous oxide in an acid solution of copper sulphate. In strongly acid solutions, the number of cuprous ions remaining in solution is limited, and when the limit is reached they are converted into cupric ions and copper, which is deposited at the cathode; whence, under like conditions, but with varying current densities, almost the same quantity of cuprous ions remain in solution. That these phenomena are not produced by the re-solution of the copper deposited at the cathode is shown by the appearance of the deposit, which is highly crystalline.

The electrolysis of copper sulphate solutions at the ordinary temperature with currents varying from 0·03 to 0·0012 ampère per 100 square centimetres was examined in a similar manner. Similar results are obtained, but smaller quantities of cuprous ions remain in the solution. With a very small current density of 0·011 ampère or less, the only effect of the current is the conversion of cupric into cuprous ions. As the current density increases, fewer cuprous ions are formed.

The agitation of the electrolyte by the hydrogen current brings some of the cuprous ions to the anode, whereby they are converted by the current into cupric ions, and consequently less copper is dissolved from the anode than that corresponding with the current; this effect is more pronounced in electrolytes suitable for the formation of cuprous ions. When the electrolyte is not stirred, more than the theoretical quantity of copper is dissolved from the anode owing to spontaneous solution.

In contradiction to the result obtained by Schuster (Abstr., 1894, 318), the authors find that copper is soluble to an appreciable extent in a solution of copper sulphate from which air is excluded. Copper foil was treated for 18 to 20 hours at the ordinary temperature, and for 2 hours at 100°, with solutions of copper sulphate similar to those employed in the electrolysis, and protected from the air by a current of hydrogen. In neutral solution, a beautiful crystalline deposit of cuprous oxide is obtained, and the copper foil increases in weight; in acid solutions (N/100 $H_2SO_4$), a decrease in weight takes place varying from 2 to 75 milligrams per 40 square centimetres of surface. The solubility increases with the concentration of the copper sulphate. Copper is quite insoluble in normal sulphuric acid at 100°.

From the above results, the authors conclude that the electrolysis of copper sulphate solutions at 100°, and at the ordinary temperature, when a small current density is employed, takes place as follows. The anode copper forms with the contiguous cupric ions cuprous ions, and the latter, under the influence of the current, are converted into cupric ions. At the cathode, the current converts the cupric ions into cuprous ions, and the latter, as soon as a certain proportion is reached,

become unstable, and are converted into cupric ions with deposition of copper or cuprous oxide.

The formation of cuprous oxide, observed with very small current density, takes place to a greater extent with high current density when the potential difference of the bath is a little above 1 volt., which voltage is necessary for the decomposition of water. The cuprous ions then unite with the hydroxyl ions to form cuprous oxide. The deposition of powdery, red copper which takes place both from neutral and acid solutions depends on the current density alone. The deposit does not contain cuprous oxide.

The formation of the black deposit which is obtained from very dilute copper sulphate solutions under a high voltage is determined by the dilution of the copper sulphate; in N/20 copper sulphate solutions, it is formed if the solution is not stirred, but on stirring, red copper is deposited; in N/100 solutions it is formed even when the solution is stirred. It is probably a compound of copper and hydrogen similar to those prepared by Mylius and Fromm (Abstr., 1894, ii, 235) by precipitating very dilute copper solutions with a more positive metal. It oxidises easily in the air with formation of water and red copper. It is also obtained from N/100 copper nitrate; if, however, a small quantity of ammonium nitrate is added and the electrolyte stirred, red copper is deposited and hydrogen evolved; with larger quantities of ammonium nitrate, red copper alone is deposited if the solution is not stirred.

Cuprous oxide is also deposited to a slight extent at the anode, and under certain conditions a yellow, amorphous precipitate is obtained, which the authors believe to be a basic cuprous sulphate.

The errors in the results obtained when a small current is measured by the copper voltameter can be eliminated to a great extent by adding alcohol to the electrolyte (Oettel, *Chem. Zeit.*, 17, 543 and 577); the alcohol decreases the concentration of the copper ions, and therefore the solubility of the copper in its sulphate solution. Very small currents can be measured with fair accuracy by this method, provided very small cathodes are employed whereby a high current density is obtained; with a current of 0·005 ampère, the error is about 0·5 per cent. Results of like accuracy are obtained by employing an electrolyte saturated with cuprous ions, which is obtained by electrolysing a 2N copper sulphate solution with 0·1 ampère at 100° for a few hours and then allowing it to cool.

In the electrolytic refining of copper, it is advantageous to heat the electrolyte to some extent; with the same current density, the deposit at the anode at 18° contained 2·9 per cent. Ag and 62·5 per cent. Cu, at 40° it contained 10·2 per cent. Ag, 1·4 per cent. Cu, and 86 per cent. Pb. The electrolyte can be heated to 50° without influencing the yield, but above this temperature the yield decreases.

The authors point out the bearing of the above results on the theory of lead accumulators, and maintain that the formation of lead peroxide at the anode is similar to the formation of cuprous ions as described above. E. C. R.

**Is a Diaphragm known that will prevent Diffusion but not the Passage of a Current?** By K. OCHS (*Chem. Centr.*, 1896, i,

289; from *Zeit. Electrotechn. und Electrochem.*, 1895, **2**, 398—402).—A diaphragm that would prevent diffusion, but would allow the passage of a current might be either—

1. A membrane not permeable by the electrolyte, but permeable by the ions; or

2. A membrane permeable by the ions, and which would absorb the electrolyte but not allow its transfusion; or

3. A membrane not permeable by either electrolyte or ions, but which allows passage of the ions when these have been deprived of their charges.

Membranes of the first class are at present unknown. Those of the second order appear to be formed by precipitation of both ions in the pores of the membrane, as, for example, in the Reynier cell (a Daniell cell in which potash replaces dilute sulphuric acid) in which copper oxide forms in the pores of the cylinder dividing the copper sulphate and potash solutions. With the continual formation of the precipitate in these cases, the resistance increases, so that any advantage obtained by the non-diffusion of the electrolyte is completely nullified. A membrane of the third order might be formed if a sufficiently thin film of mercury could be obtained, as a metal like zinc could diffuse through such a film. It does not appear, however, that such a membrane would be of any practical value. Diaphragms of the required kind for practical purposes are therefore at present unknown. H. C.

**Heats of Vaporisation of Liquids at their Boiling Points.** By MISS DOROTHY MARSHALL (*Phil. Mag.*, 1897, [v], **43**, 27—32).—The author has determined the heats of evaporation of the following liquids by the method described in a former paper (Abstr., 1896, ii, 349).

| | | | |
|---|---|---|---|
| Normal hexane ......... | L = 79·2 | Methylic iodide ......... | L = 45·9 |
| Methylic alcohol ...... | 261·6 | Ethylic iodide ......... | 47·6 |
| Formic acid ............ | 120·4 | Ethylic bromide ........ | 58·6 |
| Aniline .................. | 113·9 | Chloroform ............... | 58·4 |
| | | Carbon tetrachloride... | 46·4 |

Experiments were made to see whether an absolute determination of L might not be obtained by a modification of the method used, a knowledge of the average strength of the current and of the potential difference across the ends of the platinum spiral during boiling being alone necessary for this purpose. The results indicate that fairly accurate absolute measurements can be thus obtained. H. C.

**Determination of the Rise of the Boiling-point in Molecular Weight Determinations.** By PAUL FUCHS (*Zeit. physikal. Chem.*, 1897, **22**, 72—76).—The author describes, with the aid of diagrams, the apparatus he employs for the above purpose, and for which he claims the advantages of constancy of temperature, stability, and rapidity of working. L. M. J.

**Corresponding Temperatures.** By J. A. GROSHANS (*Ann. Phys. Chem.*, 1897, [ii], **60**, 169—173).—The author claims to have shown in 1849 that the boiling points of two substances on the absolute scale under any given pressure $p$, and under the ordinary atmospheric pres-

sure, are connected with one another by the formula $T_p/T'_p = T_{atm}/T'_{atm} = \text{const.}$

Reference is here made to determinations by Anschütz of the boiling points of 24 different organic compounds at 12 mm. and at 760 mm. pressure, and it is shown that the above formula holds with a fair degree of accuracy when water is used as a standard of comparison in each case. H. C.

**Complete Freezing Point Curves of Binary Alloys containing Silver or Copper, together with another Metal.** By CHARLES T. HEYCOCK and FRANCIS H. NEVILLE (*Proc. Roy. Soc.*, 1896, 60, 160—164).—An abstract of a paper containing the results of some experiments on the freezing points of alloys of two metals, one of the two being in each case either silver or copper. Complete freezing point curves are given in the paper for the following pairs of metals—Ag-Cu, Ag-Pb, Ag-Sn, Pb-Cu, Sn-Cu, Ag-Sb. Incomplete curves are also given showing the freezing points of dilute solutions of Bi, Au, Ni, Fe, Al in copper, and of Bi, Pt, Au, Al, and Tl in silver. From the behaviour of the more dilute solutions, the latent heat of fusion of copper was calculated as 50 cal., and that of silver as 27 cal., but both numbers can only be regarded as provisional. The eutectic alloy of silver and copper occurs exactly at the composition $Ag_3Cu_2$, but there is no other sign of chemical union between these metals. In the silver-lead and silver-tin curves, which have a good deal of likeness to each other, the eutectic alloy contains so little silver that the curve consists almost wholly of the branch starting from pure silver. The lead-copper curve affords an excellent example of the solidification of a system consisting of two conjugate liquids, a saturated solution of lead in copper, and a saturated solution of copper in lead; at from 17 to 65 atoms of lead per 100 of the alloy the freezing point remains constant at 954°. The copper-tin curve presents many singularities probably explained by the formation of compounds. The silver-antimony curve shows an angle at $Ag_3Sb$, but the eutectic point, although near $Ag_3Sb_2$, is not at this formula. It is worthy of note that in three cases an angular depression, and not a summit, occurs at a formula point.

H. C.

**Freezing Points of Binary Mixtures.** By ALBERT DAHMS (*Ann. Phys. Chem.*, 1897, [ii], 60, 119—123).—The author gives measurements of the freezing points of mixtures of acetic acid and benzene, and of acetic acid and water. The eutectic point for mixtures of acetic acid and benzene was found to be $-8{\cdot}1°$, the mixture containing 34·8 per cent. by weight of acetic acid. The eutectic point in the case of acetic acid and water was found at $-26{\cdot}55°$, when the mixture contains 58·98 per cent. by weight of acetic acid. H. C.

**Determination of the Molecular Weights of some Inorganic Substances.** By HEINRICH BILTZ (*Chem. Centr.*, 1896, i, 793; from *Math. natw. Mitt. Berlin*, 1896, 57—64).—The author has continued his determinations of the vapour densities of inorganic substances at very high temperatures (Abstr., 1896, ii, 152). The results previously obtained with arsenious anhydride were confirmed by a new set

of determinations. Selenium and tellurium at 1750—1800° have densities which accord with the molecular formulæ $Se_2$ and $Te_2$. The same formulæ were obtained by Troost and Deville at 1000° by the Dumas method, but an examination of the results of these investigators has led the author to the conclusion that they are untrustworthy. H. C.

**Racemism and the Heat Changes Produced when Liquids are Mixed. II.** By ALBERT LADENBURG (*Ber.*, 1897, **30**, 485—486. Compare Abstr., 1895, ii, 485).—When coniine is mixed with a liquid of the same specific gravity, which does not react chemically with it and does not cause contraction or expansion, no fall of temperature is observed. Thus when equal volumes of coniine and a mixture of piperidine and di-isobutylamine are brought together at 17°, a rise of 0·19° occurs, the specific gravity of the mixture being practically the same as that of its constituents. This confirms the view previously put forward by the author, that the fall of temperature observed when dextro-coniine and lævo-coniine are mixed is due to the formation of a racemic compound. A. H.

**Spontaneous Change of Oxygen into Ozone, and a Remarkable Type of Dissociation.** By WILLIAM SUTHERLAND (*Phil. Mag.*, 1897 [v], **43**, 201—214).—Bohr has placed on record a singular discontinuity in the behaviour of rarefied oxygen under a pressure of 0·7 mm., as well as a pronounced departure from Boyle's law, and Crookes, in his study of radiometer repulsion for different gases, found that oxygen at a pressure of about 0·76 mm. shows a remarkable difference from other gases, and the anomaly continues until a pressure of about $300/10^6$ to $200/10^6$ atm. is reached. The author finds that a process of association or combination of the $O_2$ molecules to form $O_3$, that is ozone, explains one of Bohr's equations and the cessation of anomaly in Crookes's experiments. It is therefore necessary in compressing pure $O_3$ that a pressure should be reached at which the $O_3$ begins to dissociate into $O_2$, and progressive increase of pressure produces progressive dissociation of $O_3$ into $O_2$. It appears that there is a certain periodic collision with one another which the $O_3$ molecules cannot stand, and this implies that the period is identical with some natural period of vibration in the molecule. This singular instance of dissociation is applied to explain the anomalous expansion of rarefied oxygen observed by Baly and Ramsay (Abstr., 1895, ii, 38), and it is pointed out that it would indicate the presence of ozone in quantity in the higher regions of the atmosphere. H. C.

**Dissociation of Chlorine Hydrate in Aqueous Solution at 0°.** By ALEXANDER A. JAKOWKIN (*Ber.*, 1897, **30**, 518—521).—The dissociation of chlorine in very dilute solutions is represented by the equation $Cl_2,Aq \rightleftarrows (HCl + HClO)Aq$, since the electrical conductivity of such solutions at 0° is equal to that of hydrochloric acid solutions containing the same amount of hydrogen chloride. According to the author, hypochlorous acid is no electrolyte. In more concentrated solutions, the conductivity of chlorine is much less.

The dissociation of bromine hydrate at 0° is extremely small, and

can only be observed in very dilute solutions. Since the dissociation of both chlorine and bromine takes place with absorption of heat, it follows that the amount of dissociation increases with the temperature. All the cases of equilibrium studied, some 150 in number, are in complete accord with the theory of electrolytic dissociation according to the equation $Cl_2,Aq = (\overset{-}{Cl} + \overset{+}{H} + HClO)Aq$. This was proved by calculating the isotherms required by the above equation when the chlorine is divided between water and carbon tetrachloride (the latter absorbs neither hydrochloric nor hypochlorous acid from aqueous solutions).

An addition of 0·5—0·1 normal hydrochloric acid completely prevents the formation of chlorine hydrate. An addition of normal or bisnormal acid, however, induces a stronger absorption of chlorine on account of the formation of $HCl_3$. J. J. S.

**Apparatus for the Rapid Determination of the Surface Tension of Liquids.** By CHARLES E. LINEBARGER (*Amer. J. Sci.*, 1896, [iv], 2, 108—122, and *J. Amer. Chem. Soc.*, 1896, 18, 514—532).—Jaeger (*Wien. Akad. Ber.*, 1891, 245) has described a method for determining the surface tension of liquids by employing two capillary tubes of different bores and measuring the difference of the depths to which they were plunged in a liquid when air forced out of them was at the same pressure. The author describes an apparatus which is a modification of the one used by Jaeger for effecting determinations in this manner. The equation which Jaeger gives for the calculation of the results appears to be merely approximate, and does not stand a severe scrutiny; a simple empirical relation was discovered, however, which brings the determinations of surface tensions by this method into agreement with those of Ramsay and Shields. This relation is $\gamma = chs + s^2$, where $\gamma$ represents the capillary constant in dynes per centimetre, $c$ the "apparatus constant," $h$ the distance between the ends of the tubes, and $s$ the specific gravity. This formula was found to stand the test of comparison with ten liquids of different properties when two sets of tubes were employed, but it is not claimed that it will furnish accurate results for any liquid whatsover, as the "apparatus constant" may differ with different liquids. H. C.

**Surface Tension of Mixtures of Normal Liquids.** By CHARLES E. LINEBARGER (*Amer. J. Sci.*, 1896, [iv], 2, 226—228).—With the apparatus described in a previous communication (preceding abstract) the author has measured the surface tensions of mixtures of some normal liquids. Solutions of toluene and ether in benzene, of turpentine, carbon bisulphide, and ethylic benzoate in toluene, and of ethylic iodide and carbon bisulphide in ether were taken. In the majority of cases, the surface tensions of normal liquids are not calculable by the rule of mixtures from the surface tensions of the pure liquids. If the observed value is greater or less than the calculated value for any one mixture of two liquids, it is also greater or less for any other mixture of the same two liquids. H. C.

**Some Thoughts about Liquids.** By CLARENCE L. SPEYERS (*J. Amer. Chem. Soc.*, 1896, 18, 724—737).—The boundary dividing

vapour from liquid is commonly supposed to be at the surface of the liquid, although the possibility of a differentiation occurring inside the liquid does not seem to be denied. The tendency for a liquid to vaporise, and the pressure of its saturated vapour, is evidently a function of temperature only. There seems to be no reason, therefore, why the fluid should not separate into vapour and liquid within the surface of the liquid.

Suppose $n$ molecules of a substance which does not dissociate on dissolving, say sugar, are dissolved in water. Let $\nu$ be the number of molecules of dissolved vapour after the $n$ molecules of substance have been dissolved, then the total number of molecules present in solution will be $\nu + n$, and the relative number of molecules of substance dissolved to the total number of molecules in solution is $n/(\nu + n)$. Let $j$ be the concentration of the dissolved vapour when alone in the liquid, and $j'$ its concentration after the new substance has been added. Since the molecule of every substance occupies the same volume, the decrease in concentration $j - j'$ will be the same whatever the substance dissolved may be, or the decrease in concentration of the dissolved vapour is proportional to the number of molecules dissolved in a certain fixed volume of solution. If the temperature be constant, the concentration of the dissolved water vapour cannot rise above the value $j$, hence the number of molecules in unit volume must be fixed, that is $\nu + n =$ constant. We have therefore $(j - j')j = a.n/(\nu + n)$, where $a$ is a constant, $j - j'$ can be calculated by van't Hoff's law, and $n$ is known, but the other quantities are not, so neither $j$ nor $\nu$ can be calculated from this equation.

The concentration of the dissolved vapour is, however, measured by its osmotic pressure. Let $\pi$ and $p$ be the osmotic pressures of the dissolved vapour and of the vapour pressure of the pure solvent respectively, and $\pi'$ and $p'$ be the corresponding quantities when a substance is in solution. Then by means of a thermodynamic cycle it may be shown that $\pi/\pi' = (p/p')x$, where $x$ denotes the number of molecules of gaseous vapour necessary to make one molecule of dissolved vapour, a quantity which the author assumes to be equal to 1. Since $j/j' = \pi/\pi'$, we have $(p - p')/p = a.n/(\nu + n)$. But this will also be equal to $n/(N + n)$, where $N$ is the number of molecules of liquid in which $n$ molecules of substance have been dissolved, for by experiment $(p - p')/p = n(N + n)$. If the value of $n$ is so small that it may be neglected in comparison with $\nu$ and $N$, we get $a.n/\nu = n/N$, or $a = n/N$. From this we have

$$\frac{\nu}{N} \quad \frac{n}{\nu + n} = \frac{n}{N + n} \quad \text{or} \quad \nu = N,$$

that is, the concentration of the dissolved vapour is the same as the concentration of the liquid, or in other words, all the solvent is to be considered as dissolved vapour. This is, in effect, the same conclusion that van der Waals reached by a very different method in his celebrated treatise.

A liquid is to be looked on, then, as a condensed gas, not simply condensed in the sense that it is matter compressed into smaller space, but condensed in the sense that the gaseous activity, pressure, is carried into the liquid condition, and we are to treat a liquid as

we would a gas. A substance dissolved is simply brought into the same condition that the liquid is in, and consequently should have the same property of exerting an osmotic pressure that the liquid has.

H. C.

**Determination of the Diffusion Coefficients of some Gases in Water.** By C. Gustav Hüfner (*Ann. Phys. Chem.*, 1897, [ii], 60, 134—168).—The author draws attention to the fact that, since Stefan showed in 1878 that Fick's law of diffusion holds in the case of carbonic anhydride in water or alcohol, no determinations of the rates of diffusion of gases in liquids have been made, with the exception of Müller's experiments on ammonia in water and alcohol (Abstr., 1891, 1147). Experimental difficulties account in some measure for this fact, since, if the gas is placed above the liquid, as it dissolves the liquid becomes heavier and sinks, and so produces currents which disturb the regular course of the diffusion, a difficulty only to be avoided by the use of tubes of very small bore. In order to place the liquid above the gas and so prevent the formation of concentration currents, the author uses a tube divided into two portions by means of a thin plug of hydrophane, placing water in the upper portion of this tube, and then allowing the gas to diffuse through the hydrophane into the water. Taking the day as unit of time and the centimetre as unit of length, if $k$ is the coefficient of diffusion, $k = vl/a$, where $v$ is the volume of gas measured at 0° and 760 mm. that will diffuse under a pressure of 1 atm. through a column of water 1 cm. in length and 1 cm.$^2$ in area, and $a$ is the coefficient of absorption of the gas. Exner has shown that the interchanging volumes of two gases, separated from one another by a soap film, are proportional to their coefficients of absorption and inversely proportional to the square roots of their densities. With the aid of Stefan's value for the diffusion coefficient of carbonic anhydride in water and the known densities of the different gases, it is possible therefore to calculate the coefficients of diffusion for gases, as these should be inversely proportional to the square roots of their densities. In the following table are given the numbers thus calculated and the numbers obtained for the temperature 16°, taking Stefan's value for $k$ in the case of carbonic anhydride at 1·38, and using this as the basis in the calculations.

| | $k_{cal.}$ | $k_{obs.}$ |
|---|---|---|
| Carbonic anhydride | (1·38) | 1·37 |
| Hydrogen | 6·47 | 4·09, 4·45, 7·53 |
| Oxygen | 1·62 | 1·62 |
| Nitrogen | 1·73 | 1·73 |
| Nitrous oxide | 1·34 | 1·35 |
| Chlorine | 1·087 | 1·098 |

The agreement obtained in the above cases is not found when the value of $k$ for ammonia is taken from Müller's experiments, as in this case the calculated value for $k$ is 2·22 and the observed value is found to be 15·96.

H. C.

**Attempt to Determine the Adiabatic Relations of Ethylic Oxide.** By Edgar P. Perman, William Ramsay, and J. Rose-Innes (*Proc. Roy. Soc.*, 1896, 60, 336—337).—The wave-length of sound in

gaseous and in liquid ethylic oxide was determined by the Kundt method, between limits of temperature ranging from 100° to 200°, and of pressure ranging from 4000 mm. to 31,000 mm. of mercury, and of volume ranging from 2·6 c.c. per gram to 71 c.c. per gram. Ramsay and Young showed that for ether (and some other liquids) a linear relation subsists between pressure and temperature, volume being kept constant, so that $p = bT - a$. It has been found that a similar relation obtains between adiabatic elasticity and temperature, volume, as before, being kept constant; so that, within limits of experimental error, if $E$ stands for adiabatic elasticity, $E = gT - h$, where $g$ and $h$ are functions of the volume only. Between these two equations, we may eliminate $T$, and so express $E$ as a linear function of $p$, volume being kept constant. The coefficient of $p$ in such an equation would be $g/b$, and this fraction, on being calculated from the data available, proves to be nearly constant. If $g/b$ is treated as strictly constant, it is possible to integrate the resulting differential equation, and from the complete primitive to draw a set of adiabatic curves, this being the first time that adiabatic curves have been obtained for any substance except perfect gases. H. C.

**Solubility of Hydrated Mixed Crystals.** By Willem Stortenbeker (*Zeit. physikal. Chem.*, 1897, **22**, 60—71).—The crystallisation of solutions containing zinc and copper sulphates was investigated in the endeavour to obtain experimental proofs of the views published in the author's previous paper (Abstr., 1896, ii, 13). The results obtained were: (1) Solutions containing 21·5—100 per cent. mols. of copper sulphate crystallise in triclinic crystals with but little zinc, yielding by recrystallisation almost pure copper sulphate. (2) Solutions of 8·4—21·5 per cent. mols. of copper sulphate gave monoclinic pseudo-rhombohedra with $7H_2O$, the composition of which differs but slightly from that of the solution. (3) Solutions of 0—8·4 per cent. mols. of copper sulphate give rhombic crystals with little copper, yielding by re-crystallisation almost pure zinc sulphate. These results are expressed in the accompanying table, together with Retgers' values, the number giving the percentage of copper sulphate.

| | Rhombic. | Monoclinic. | Triclinic. |
|---|---|---|---|
| Solutions ........ ...... | 0—8·36 | 8·36—21·5 | 21·5—100 |
| Crystals ............... | 0—1·97 | 14·9 —31·9 | 82·9—100 |
| Crystals (Retgers) ...... | 0—2·34 | 16·8 —34·6 | 92·1—100 |

The solubility isothermal, therefore, consists of three portions, and examples were obtained of each of the labile states, crystals being obtained having the composition represented by each portion of the curve. L. M. J.

**Solid Solutions.** By Giacomo L. Ciamician and Felice Garelli (*Zeit. physikal. Chem.*, 1897, **22**, 134—135).—With respect to Bodländer's deductions from their work (this vol., ii, 133), the authors point out that his conclusions regarding the formation of a solid solution of salicylic

and benzoic acids had been anticipated by them, and further, the correct method of determining the partition ratio had been employed by them in their paper. L. M. J.

**Constitution of Salt Solutions.** By HEINRICH LEY (*Zeit. physikal. Chem.*, 1897, 22, 77—84).—The colour of a solution of cupric chloride changes from blue to green when the solution is heated, the temperature at which the change occurs increasing with the concentration, and according to the hydrate theory this change is due to the passage from the hydrate $CuCl_2,3H_2O$ to $CuCl_2,2H_2O$. The latter salt, however, is not green, but blue, the ordinary green colour being due to a superficially condensed solution, and the author regards the colour change as due to a change in the degree of dissociation of the compound. Measurements of the electrical conductivity at temperatures varying from 18·7° to 80° showed the increase to be perfectly regular with no breaks in the curve, and the value $d\lambda/dT$ to decrease from 0·9 to 0·66. In solvents other than water, the colour varies, being green in alcohol, yellowish-green in acetone, yellow in urethane, and blue in pyridine. The determination of the molecular weight in these solutions gave values, 133—136 in alcohol, and 164—194 in acetone, the conductivity being $\lambda_{16} = 2·16$ and 6·1, whilst in pyridine $\lambda_{30} = 0·05$, so that the blue colour of the pyridine solution is not due to copper ions, but to an undecomposed cupric chloride-pyridine compound. L. M. J.

**Isomorphous Mixtures.** By HERMANN AMBRONN and MAX LE BLANC (*Zeit. physikal. Chem.*, 1897, 121—131).—A controversial paper in which the authors uphold their views against those of Küster (Abstr., 1895, ii, 257), regarding isomorphous mixtures as mixtures in which no molecular interpenetration occurs. L. M. J.

**False Equilibria of Hydrogen Selenide.** By H. PÉLABON (*Compt. rend.*, 1897, 124, 360—363).—The author has determined the respective limits of direct formation and of decomposition of hydrogen selenide when the substances are maintained at given temperatures for comparatively long periods, such as 20 or 40 days. The lowest temperature at which any direct formation of hydrogen selenide was observed is 250°. The results are represented by two curves, and the area between them corresponds with Duhem's "region of false equilibria." The two curves are further apart the lower the temperature, and they are each further from the curve of true equilibria the lower the temperature. Both, however, merge into the curve of true equilibria at temperatures which approximate to 320°. Above 325°, the limits of formation and decomposition coincide. C. H. B.

**Third Annual Report of Committee on Atomic Weights.** By FRANK W. CLARKE (*J. Amer. Chem. Soc.*, 1896, 18, 197—214).—A summary of atomic weight determinations published during 1895, with a complete *table of atomic weights recalculated from all available data.* H. C.

**A New Form of Vacuum Pump.** By J. WETZEL (*Ber.*, 1897, 30, 537—538).—In this pump, a drawing of which is given in the paper, a bulb having a narrow outlet is blown on the tube imme-

diately under the injector; by this means, the effective action of the pump is doubled, whilst less water is used than in the ordinary form. Since, also, the time occupied in exhaustion is shorter, this pump is especially adapted for distillation under diminished pressure.

J. F. T.

## Inorganic Chemistry.

**Decomposition and Formation of Hydrogen Iodide.** By MAX BODENSTEIN (*Zeit. physikal. Chem.*, 1897, **22**, 1—22).—The author's previous experiments on this subject (Abstr., 1893, ii, 369; 1894, ii, 12) were not in complete accord with theoretical deductions, and they were therefore repeated with very great experimental precautions. It was found that when hydrogen and iodine combine, the quantity of hydrogen iodide found by titration with sodium hydroxide did not correspond with that calculated from the loss of hydrogen and iodine, whilst the difference between the two values was almost independent of the quantity of gases employed and of the duration of the experiment. This, the author considers, is due to the combination of the iodide with the alkali of the glass, and experiments indicated an approximate proportionality between the surface area of the glass and the loss of iodide. In the experiments, this must be allowed for, and when the correction is made, the apparent increase of decomposition with pressure (Abstr., 1894, ii, 12) is not found to exist. The mean values for the amounts of iodide decomposed at the boiling points of sulphur and mercury were found to be 0·2198 and 0·1946, the corresponding values for the equilibrium constant, $K = C_I C_H / C^2_{HI}$, being 0·0212 and 0·0176; the individual results, however, varied considerably. The velocity constant, as calculated for the bimolecular reaction $2HI \leftrightarrows H_2 + I_2$, gave the following values.

| | ½ atm. | 1 atm. | 1½ atm. | 2 atm. |
|---|---|---|---|---|
| Sulphur vapour ......... ... . | 0·00278 | 0·00563 | 0·00867 | 0·01223 |
| Mercury vapour ............... | 0·0000362 | 0·0000748 | 0·0001221 | 0·0001647 |

The values are approximately proportional to the pressure, and this obtains theoretically in the case of bimolecular reactions. Other experiments were initiated to test whether a minimum decomposition exists at 320°, as indicated by the earlier experiments (*loc. cit.*), but the results are not yet available. L. M. J.

**Decomposition of Hydrogen Iodide by Light.** By MAX BODENSTEIN (*Zeit. physikal. Chem.*, 1897, **22**, 23—33).—The author has investigated the decomposition of hydrogen iodide by light, and finds that the equation, $dx/dm = k\,(1 - x)$, leads to an approximately constant value for $k$ ($m$ = light intensity $x$ time). The reaction is therefore unimolecular, not bimolecular, and is represented by the equation

HI = H + I, and differs, therefore, from the decomposition induced by high temperatures (preceding abstract). Hence the action of light, in the author's opinion, does not render the whole volume of gas more capable of decomposition, but each light ray of the necessary intensity decomposes into its elements the molecules of hydrogen iodide in its path. L. M. J.

**Atmospheric Ozone on Mount Blanc.** By MAURICE DE THIERRY (*Compt. rend.*, 1897, **124**, 460—463).—In August, 1896, the air at Chamounix at a height of 1050 metres was found to contain 3·5 to 3·9 milligrams of ozone in 100 cubic metres of air. At the Grands Mulets, at a height of 3020 metres, the quantity found 10 days later was 9·4 milligrams in 100 cubic metres. These numbers are much higher than the quantities found at Mountsouris (1·9 to 4·0), and it seems clear that the proportion of ozone increases with the altitude. The estimations were made by passing the air through a standard solution of sodium arsenite containing potassium iodide free from iodate.

C. H. B.

**Production of Active Oxygen by the Slow Oxidation of Triethylphosphine and of Benzaldehyde.** By W. P. JORISSEN (*Zeit. physikal. Chem.*, 1897, **22**, 34—53).—During the slow oxidation of many substances in air or oxygen, a portion of the oxygen is changed into an active modification. In the case of phosphorus, 2 atoms of phosphorus renders active 1 atom of oxygen (Abstr., 1895, ii, 212 and 262), and the author's experiments were conducted with the object of determining the corresponding ratio in the case of triethylphosphine and of benzaldehyde. The first compound was found, by oxidation in air, to require more oxygen than that theoretically necessary for conversion into triethylphosphine oxide, and this was found to be due to the formation of small quantities of ethylic diethylhypophosphite. The results were no simpler when air at low pressure was employed, but in the presence of excess of water, the oxidation was found to proceed in such a manner as to produce nothing but the phosphine oxide. The active oxygen was determined by the use of commercial sodium indigosulphonate, and numerous experiments proved that the quantity is equal to that required for the oxidation.

Benzaldehyde, by slow oxidation, passes completely into benzoic acid, the action being greatly accelerated by light, although it proceeds also in darkness. In this case also, the quantity of oxygen required for oxidation is equal to that rendered active. Analogous results, in the case of the oxidation of metals, had been previously obtained by Schönbein, Träube (Abstr., 1893, ii, 412), and Bodländer. The opinions of various chemists on this action are reviewed, and the author considers his own results to be in complete agreement with the views expressed by Van't Hoff (Abstr., 1895, ii, 262). L. M. J.

**So-called 'Autoxidation.'** By RUDOLF IHLE (*Zeit. physikal. Chem.*, 1897, **22**, 114—120).—The oxidising power of water containing dissolved air is greatly affected by the dissolution in it of various salts; thus, in solutions of hydroxides, carbonates, phosphates, borates, and nitrites, metals remain bright for a considerable period, although they

rapidly tarnish in pure water or solutions of chlorides, bromides, iodides, nitrates, &c. The author considers the oxidation to be due to the union of the metallic ions with negative hydroxyl ions resulting in the formation of a hydroxide, the ionisation of more metal and production of more hydroxyl by the dissolved oxygen. The accelerative influence of the neutral salts is a catalytic action similar to their effect on sugar inversion. The potential of the oxygen, and hence its tendency to form hydroxyl ions, is dependent on the concentration of these already present in the liquid, and is therefore diminished by the dissolution of salts which yield OH ions. The course of the reaction may probably be represented thus: $M'' + 2OH{\cdot}H = M(OH)_2 + H_2$; $H_2 + O_2 = H_2O_2$; $M + H_2O_2 = M(OH)_2$. This view is supported by the fact that the addition of hydrogen peroxide acts similarly to air or oxygen. Owing to the peculiar dissociation of hydrogen peroxide, it acts as an oxidising or a reducing agent. Thus in acid solution its potential (against bright platinum) is $-1{\cdot}078$, and in alkaline solution $-0{\cdot}367$, and hence substances whose potentials lie between these limits would be oxidised in acid solution and reduced in alkaline, examples of such actions being given. L. M. J.

**Pyrosulphuryl Chloride.** By J. ADOLPHE BESSON (*Compt. rend.*, 1897, **124**, 401—403).—Pyrosulphuryl chloride partially decomposes when boiled under ordinary pressure, but it can be fractionated under reduced pressure, and boils at 53° under a pressure of 15 mm., whilst sulphuric monochlorhydrin boils at 65° under the same pressure. It can be freed from chlorine by agitation with mercury, care being taken to keep the temperature well below 60°. Sulphuric anhydride and sulphuric monochlorhydrin are removed by adding phosphorus pentachloride in excess, and the pyrosulphuryl chloride is then readily purified by fractionation. When pure, it boils at 142—143° under a pressure of 765 mm., and when strongly cooled forms a white, crystalline solid which melts at −39°. Pure sulphuric monochlorhydrin boils at 152° under a pressure of 765 mm., and does not solidify at −75°.

Attempts to obtain pyrosulphuryl chloride by heating sulphuryl chloride and sulphuric anhydride at 100°, or by subjecting them to prolonged exposure to sunlight, were unsuccessful. Dry hydrogen bromide acts on the chloride at 50° with liberation of sulphurous anhydride and bromine and formation of sulphuric monochlorhydrin, the latter being in its turn completely decomposed by prolonged action of the hydrogen bromide, $2SO_2(OH)Cl + 2HBr = Br_2 + 2HCl + SO_2 + H_2SO_4$. Hydrogen iodide acts on the chloride cooled in a mixture of ice and salt, the products being the same as with hydrogen bromide, together with some hydrogen sulphide and sulphur. Hydrogen sulphide acts slowly on pyrosulphuryl chloride in the cold, the principal reaction being $S_2O_5Cl_2 + H_2S = S + 2HCl + SO_3 + SO_2$; on heating the reaction, $3S_2O_5Cl_2 + 2H_2S = S_2Cl_2 + HCl + 3SO_2 + 3SO_2(OH)Cl$, which is secondary in the cold, becomes the chief or even the only reaction. Dry hydrogen phosphide also decomposes the chloride at the ordinary temperature, metaphosphoric acid and the sulphide $P_4S_3$ being amongst the products. C. H. B.

**Action of Dilute Nitric Acid on Nitrates in Presence of Ether.** By CHARLES TANRET (*Compt. rend.*, 1897, **124**, 463—466).—When water containing nitric acid is agitated with aqueous ether, the acid is divided between the water and the ether in a constant ratio which is independent of the relative volumes of the two liquids, but varies with the temperature and concentration. The following coefficients were observed.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Nitric acid in 100 ...... | 0·25 | 0·50 | 1·0 | 2·0 | 10·0 | 18—40 | 45 |
| Coefficient of division... | 1 : 160 | 1 : 100 | 1 : 66 | 1 : 42 | 1 : 17 | 1 : 12 to 1 : 10 | 1 : 8·5 |

In presence of soluble nitrates, these coefficients are much higher, and increase with increasing quantities of a given nitrate, but vary also with equal quantities of different nitrates. With 5 grams of dry nitrate dissolved in 20 c.c. of nitric acid of 1 : 100, the coefficients vary in a noteworthy manner. For metals of the same or neighbouring families, the coefficients fall as the atomic weights rise, whilst at the same time they are inversely proportional to the weight of the metal contained in the nitrates. If, however, the coefficients are considered with respect to the weight of the radicle $NO_3$ contained in the nitrates, curious geometric progressions are observed with the alkali metals, the metals of the alkali earths, lead and thallium, and zinc and cadmium.

The effect of the nitrates may be due to two causes. Acid nitrates may be formed, the dissociation of which may be limited by the increasing quantity of normal salt added, these acid nitrates being afterwards dissociated by the ether, which takes up part of the acid. When large quantities of nitrates are added, they may form hydrates with part of the water, and thus increase the concentration of the acid and thereby raise the coefficient. C. H. B.

**Nitrogen Sulphide.** By WILHELM MUTHMANN and E. SEITTER (*Ber.*, 1897, **30**, 627—631. Compare Abstr., 1896, ii, 298).—The *tetrachloride* of nitrogen sulphide, $N_4S_4Cl_4$, was first obtained by Demarçay (Abstr., 1881, 346) on suspending nitrogen sulphide in chloroform and passing dry chlorine through the liquid; it is excessively unstable, and when exposed to moist air, rapidly becomes converted into a black, tarry mass.

*Thiotrithiazyl chloride*, $N_3S_4Cl$, is obtained from nitrogen sulphide by the action of warm sulphur dichloride diluted with chloroform; it is more conveniently prepared by heating nitrogen sulphide with acetic chloride (4 parts) in a reflux apparatus for half an hour, when it is obtained as an intensely yellow, crystalline powder, exhibiting the properties attributed to it by Demarçay. On boiling the substance with alcohol during a short period, and treating the liquid with a few drops of alcoholic potash, an intense, violet-red coloration is developed, and does not immediately disappear on dilution with water. Ammonia gas is rapidly absorbed by the dry compound, which explodes violently after a few minutes; if thiotrithiazyl chloride is suspended in chloroform and submitted to the action of the gas, the liquid becomes orange-red, and ammonium chloride and sulphide are produced, nitrogen sulphide being regenerated.

*Thiotrithiazyl nitrate*, $N_3S_4NO_3$, is produced on dissolving the chloride in highly concentrated nitric acid and evaporating the yellow liquid

in a vacuum; the substance, which is very explosive, crystallises in beautiful, sulphur-yellow, transparent prisms 1 cm. in length, and when preserved during some days becomes opaque and acquires the odour of sulphurous anhydride and oxides of nitrogen. The solution in water is yellow and transparent, but becomes opaque in a few minutes, depositing a black substance mixed with much sulphur; a red liquid is obtained on boiling the compound with alcohol.

*Thiotrithiazyl bromide,* $N_3S_4Br$, obtained by dissolving nitrogen sulphide and sulphur dibromide (5 parts) in carbon bisulphide, crystallises in small, yellow needles; it is also formed when excess of bromine acts on thiotrithiazyl chloride in warm carbon bisulphide, and is identical with the compound produced on exposing the tetrabromide of nitrogen sulphide to the action of moist air (compare Clever and Muthmann, *loc. cit.*). The substance is stable in air, and when water is boiled with it, ammonium bromide, sulphur, and sulphurous anhydride are produced; hot dilute alkalis give rise to ammonia, along with alkali bromide, thiosulphate, and sulphide.

*Thiotrithiazyl iodide,* $N_3S_4I$, is prepared by dissolving thiotrithiazyl chloride in ice cold water and immediately adding excess of an ice cold solution of potassium iodide; it is a dark red, crystalline powder which decomposes spontaneously on exposure to the air, vapours of iodine being evolved. The compound is also obtained by acting on the chloride with iodine dissolved in methylic alcohol, but it invariably contains chlorine when prepared in this way.

*Thiotrithiazyl thiocyanate,* $N_3S_4CNS$, is obtained by adding a solution of potassium thiocyanate to an ice cold solution of thiotrithiazyl chloride or nitrate; it crystallises in lustrous, bronze leaflets and resists the action of air. The salt dissolves somewhat readily in benzene and chloroform.

The authors regard these compounds as containing a radicle composed of sulphur and nitrogen, and having the formula $N_3S_4$; from this point of view, the salts have the constitutional formula

$$S_2{<}\begin{matrix}N\cdot S\\N\cdot S\end{matrix}{>}N\cdot X.$$

M. O. F.

**Metaphosphoric Acid.** By MARCELLIN P. E. BERTHELOT and GUSTAVE ANDRÉ (*Compt. rend.*, 1897, **124**, 265—269).—Metaphosphoric acid, when dissolved in water, changes mainly into orthophosphoric acid, the quantity of pyrophosphoric acid that is formed being always very small. Sodium metaphosphate in aqueous solution gradually becomes acid owing to its conversion into orthophosphate and pyrophosphate. Metaphosphate that has been prepared at 280° changes somewhat rapidly, but that prepared at a high temperature alters very slowly at the ordinary temperature, provided neither acid nor alkali is present. In the case of the former, about 45 per cent. is converted into the ortho-salt in the act of dissolution, and afterwards the change is more gradual. Metaphosphoric acid, prepared by the dehydration of the ortho-acid, behaves similarly when dissolved in water; the change is at first rapid and afterwards becomes more gradual, but the rate of change increases with the concentration of the solution.

In any case, the method described (this vol., ii, 283) for the estima-

tion of pyrophosphoric acid is not applicable to its separation from metaphosphoric acid, because the latter yields the same precipitate when treated in the same way. C. H. B.

**Sulphoxyarsenates [Thioarsenates].** By R. F. Weinland and O. Rumpf (*Zeit. anorg. Chem.*, 1897, 14, 42—65. See also Abstr., 1896, ii, 473).—Sodium monothioarsenate, $Na_3AsSO_3,12H_2O$, prepared by the method previously described, crystallises in colourless, transparent crystals belonging to the rhombic system

$$[a : b : c = 0{\cdot}9199 : 1 : 0{\cdot}6602].$$

This salt is also obtained together with the dithioarsenate by boiling an aqueous solution of sodium arsenite with sodium polysulphide, and also by boiling sodium arsenite with sodium monosulphide; in the latter case, however, the dithioarsenate and tetrathioarsenate $Na_3AsS_4$ are also formed. The mixed salts, which have a composition similar to Geuther's sodium trisulphoxydiarsenate and to Preis's sodium pentasulphoxytetrarsenate, are separated by fractional precipitation with alcohol.

The formation of sodium monothioarsenate from sodium arsenite and sulphur, and the gradual decomposition of free monothioarsenic acid into arsenious acid and sulphur, is very similar to the formation of sodium thiosulphate and the decomposition of thiosulphuric acid. On the other hand, the authors were unable to obtain sodium monothioarsenate by the action of iodine on a mixture of sodium arsenite and sodium monosulphide, neither were they able to obtain a compound similar to sodium tetrathionate by the action of iodine on sodium monothioarsenate. It is probable, therefore, that monothioarsenic acid contains 3 hydroxyl groups, the sulphur being united to the arsenic atom by both bonds. Sodium monothioarsenate gradually effloresces on exposure to the air; it may be boiled in aqueous solution without decomposition, but when the solution is heated in a sealed tube at 150°, it yields sodium arsenate and sodium tetrathioarsenate. If boiled with concentrated sodium hydroxide, it undergoes but very slight decomposition, although the mixture, if evaporated to dryness, yields sodium sulphide, sodium arsenate, and much undecomposed monothioarsenate. It is also stable towards sodium hydrogen sulphide and sodium sulphide, but when boiled with sodium bisulphide it is converted into sodium dithioarsenate and arsenate. A boiling, concentrated, aqueous solution of the salt dissolves a small quantity of sulphur, which, however, separates completely as the solution cools.

Sodium monoselenoarsenate, $Na_3AsSeO_3 + 12H_2O$, prepared in a manner similar to the preceding salt, crystallises in colourless, transparent, rhombic crystals which are isomorphous with the preceding salt [$a : b : c = 0{\cdot}9284 : 1 : 0{\cdot}6409$]. When pure, it is fairly stable on exposure to air, but gradually becomes covered with a red skin of selenium; exposure to direct sunlight completely decomposes it. In aqueous solution, it is partially decomposed into selenium and arsenious acid at the ordinary temperature, more quickly on heating; a complete and immediate decomposition takes place on the addition of hydrochloric acid.

The corresponding tellurium compound was not obtained pure, as the product is decomposed by water with separation of tellurium.

Potassium monothioarsenate, $K_3AsSO_3 + 2H_2O$, is obtained in a crude state in a similar manner to the sodium salt, but the pure salt is most conveniently prepared by dissolving potassium dihydrogen monothioarsenate in concentrated potassium hydroxide free from carbonate, and allowing the mixture to crystallise by spontaneously evaporating over sulphuric acid and potassium hydroxide; it crystallises in colourless prisms. The *ammonium* salt $(NH_4)_3AsSO_3 + 3H_2O$, which is obtained together with the arsenate and tetrathioarsenate, is separated by fractional precipitation with alcoholic ammonia; it crystallises in small, lustrous leaflets. The *barium* salt crystallises with $6H_2O$; it is prepared by precipitating a solution of the sodium salt with barium chloride. The *sodium barium* salt, $NaBaAsSO_3 + 9H_2O$, is obtained by adding barium chloride to a solution of the sodium salt until a permanent precipitate ceases to be formed; it crystallises in small, colourless cubes or hollow, four-sided pyramids. The corresponding *sodium barium monoselenoarsenate*, obtained in a similar way, crystallises in four-sided prisms.

Monosodium monothioarsenate, $NaH_2AsSO_3$, obtained as previously described by the action of salicylic acid (2 mols.) on the trisodium salt, crystallises in microscopic, colourless prisms; it reddens litmus, decomposes into sodium arsenite, sulphur, and water if kept in a closed vessel or when treated with water, and is converted into the trisodium salt on treatment with concentrated sodium hydroxide. The monopotassium salt, obtained by treating the crude tripotassium salt with salicylic acid, crystallises in short needles; the *dipotassium* salt, $K_2HAsSO_3 + 2\frac{1}{2}H_2O$, in colourless, prismatic needles.

Sodium dithioarsenate, $Na_3AsS_2O_2 + 10H_2O$, is obtained by the methods previously described. It is not decomposed by boiling with sodium hydroxide, and only partially so when evaporated to dryness; when heated in a sealed tube at 150° with sodium hydroxide, it yields arsenate and tetrathioarsenate. No precipitate is formed on adding barium chloride to a hot dilute solution of the salt, but, on cooling, a precipitate of lustrous spangles gradually forms. The *potassium* salt, prepared by boiling the tetrathioarsenate with potassium hydroxide, forms small, yellow crystals, is very hygroscopic, and is decomposed by water, yielding potassium arsenate and tetrathioarsenate. E. C. R.

**Homogeneity of Helium and Argon.** By WILLIAM RAMSAY and J. NORMAN COLLIE (*Proc. Roy. Soc.*, 1896, 60, 206—216).—See Abstr., 1896, ii, 647.

**Attempt to Separate the Two Constituents of Clèveite Gas by Diffusion.** By AUGUST HAGENBACH (*Ann. Phys. Chem.*, 1897, [ii], 60, 124—133).—Helium obtained from clèveite by the action of sulphuric acid on the mineral was submitted to diffusion through a plug of graphite, with the object of effecting a separation of the gas into its two supposed constituents. Spectroscopic examination of the gas as it diffuses through the graphite shows that the yellow $D_3$ line makes its appearance first of all in the spectrum, and some seconds later the green helium line appears. It is impossible to decide definitely, how-

ever, whether this behaviour is due to diffusion or to the change in the pressure to the gas. Helium was also allowed to diffuse through unglazed porcelain, and the densities of the original gaseous mixture, of the diffusate, and of the residue were determined. The following results were obtained.

| | Weight in milligrams. | Volume in c.c. at 0° and 760 mm. | Density, H = 1. |
|---|---|---|---|
| Gaseous mixture ... | 20·80 | 138·20 | 2·315 |
| Diffusate ............ | 8·20 | 44·84 | 2·032 |
| Residue ............... | 10·07 | 86·60 | 2·576 |

The author concludes from the results of his experiments that a separation of clèveite gas into two constituents has been effected. (Compare Ramsay and Collie, Abstr., 1896, ii, 645.) H. C.

**Argon, Helium, and Prout's Hypothesis.** By Bohuslav Brauner (*Chem. News*, 1896, **74**, 223—224).—The author inclines to the view that argon and helium are allotropic states of nitrogen and hydrogen of a peculiar and entirely novel character, and suggests that determinations of their specific and atomic heats would throw important light on this question. H. C.

**Ammonio-silver Chlorides.** By R. Jarry (*Compt. rend.*, 1897, **124**, 288—291).—When an ammoniacal solution of silver chloride is placed in a vacuum, it behaves, at first, like a solution of ammonia only, and the pressure diminishes as the ammonia is removed. When, however, the pressure is reduced to 268 mm., it remains stationary for a time, and 10 to 15 c.c. of liquid may give off 500 c.c. of ammonia without any change of pressure. Beyond this point, the pressure again diminishes gradually until it reaches 17 mm., when it again remains stationary. When the vapour pressure of water is taken into account, these pressures become 263 mm. and 12 mm. respectively. Now these are exactly the respective dissociation pressures of the compounds $AgCl,3NH_3$ and $2AgCl,3NH_3$ at 0° in a dry vacuum, and it follows that the two compounds are successively formed under the conditions specified, and have the same dissociation pressures in solution as in a dry vacuum. This conclusion is confirmed by the solubility of silver chloride in ammonia solution of various degrees of concentration. The following table gives the amounts of ammonia and silver chloride respectively in 10 c.c. of liquid at 0°:

| | | | | | | |
|---|---|---|---|---|---|---|
| $NH_3$......... | 0·145 | 0·294 | 0·560 | 0·624 | 1·177 | 1·636 |
| AgCl ...... | 0·049 | 0·136 | 0·344 | 0·400 | 0·468 | 0·518 |
| $NH_3$......... | 2·816 | 2·980 | 3·019 | 3·243 | 3·456 | 3·748 |
| AgCl ...... | 0·659 | 0·709 | 0·725 | 0·587 | 0·477 | 0·390 |

If these results are plotted with the weights of ammonia as abscissæ and the weights of silver chloride as ordinates, the curve shows marked discontinuity at a point which corresponds with the formation of $2AgCl,3NH_3$ (allowance being made for the quantity of ammonia necessary to saturate the water present under a pressure of 12 mm.), and a second break at a point which corresponds with the formation of $AgCl,3NH_3$. Below the first point, the curve represents the solubility

of silver chloride only, between the two points it represents the solubility of the compound $2AgCl,3NH_3$, and beyond the second point the solubility of the compound $AgCl,3NH_3$ under pressures higher than its dissociation pressure.

Other conditions being the same, the solubility of silver chloride in ammonia increases with the temperature; a solution saturated at 20° and cooled to 0°, deposits crystals of the compound $2AgCl,3NH_3$. Highly concentrated solutions deposit the compound $AgCl,3NH_3$. If the solution is represented by a part of the curve beyond the second break, precipitation of the salt is produced by passing a current of ammonia gas into it; if it is represented by a part of the curve between the two breaks, precipitation follows a reduction of the pressure.

C. H. B.

**Silver Peroxynitrate.** By EDUARD MULDER and J. HERINGA (*Rec. Trav. Chim.*, 1896, **15**, 235—279. Compare Abstr., 1896, ii, 561).—Further quantities of Ritter's black compound have been obtained from solutions of silver nitrate containing from 100 to 1000 grams of the salt per litre, and the authors have succeeded in establishing the anhydrous character of the compound; the different amounts of water given by other experimenters were due in all probability to the fact that, on heating, the compound may explode, and particles can thus pass into the drying tubes. The strength of the original solution appears to have little or no influence on the composition of the black product formed; further analyses agree with the formula, $2Ag_3O_4,AgNO_3$, previously given. More accurate results are obtained when the nitrogen is estimated as silver nitrate rather than as nitrogen by Dumas's method.

The compound slowly undergoes decomposition at the ordinary temperature, whilst, on warming suddenly, oxygen is evolved almost explosively; this oxygen the authors term *oxygen excess*, the amount being 5 atoms for each molecule of the compound. Part of the oxygen excess appears to be given off more readily than the remainder. The residue left consists of a mixture of silver oxide and nitrate, which are best separated by water and not by alcohol. The paper concludes with a short history of the compound.

J. J. S.

**Solubility of Calcium Carbonate and Phosphate.** By EGIDIO POLLACCI (*L'Orosi*, 1896, **19**, 217—230).—Red litmus paper turns blue when placed in a sludge of pure calcium carbonate, and on leaving pure calcium carbonate in contact with water free from carbonic anhydride for 24—30 hours and filtering, the filtrate has an alkaline reaction towards litmus; on boiling calcium carbonate with water and rapidly filtering, the filtrate slowly deposits calcium carbonate. The author finds that calcium carbonate dissolves in 9662 parts of water at 12°, and in 6904 parts at 100°; Fresenius determined these numbers as 10,601 and 8234 respectively.

One litre of rain water dissolves 0·0216 gram of tricalcium phosphate at 12·5° and 0·0120 gram at 100°; if the water be saturated with carbonic anhydride, it dissolves 0·1605 gram of phosphate at 10·5°. One litre of rain water free from air and carbonic anhydride dissolves 0·0098 gram of the phosphate at 12·5°, but if the phosphate be dried at

25° instead of moist as precipitated, 0·0181 gram is dissolved. Water saturated with carbonic anhydride dissolves 0·0450 gram of calcium phosphate and 0·3650 gram of calcium carbonate per litre at 13·5° if agitated with a mixture of the salts.

Since many plants contain much lime, a constituent in which many earths are poor, the author recommends that calcium salts, such as the sulphate or carbonate, and lime should be applied as a manure, as the addition of these substances may sometimes give better results than that of calcium phosphate. W. J. P.

**The So-called "Hypoiodite of Magnesia."** By JAMES WALKER and SYDNEY A. KAY (*Proc. Roy. Soc. Edin.*, 1896, 235—248).—When magnesia is shaken up with iodine, it unites with the latter and assumes a deep brown colour (Gay-Lussac). The same brown colour is produced, whether the magnesia is freshly precipitated, dried at 100°, or ignited over the blow-pipe, and whether the iodine is in the form of vapour, or in solution in water, aqueous potassium iodide, chloroform, carbon bisulphide, or alcohol. Traces of iodine vapour are given off from the brown substance, even at the ordinary temperature, but heating for several hours at 350° is not sufficient to expel all the iodine. At a red heat, iodine is given off rapidly, and magnesia remains. Chloroform, carbon bisulphide, and carbon tetrachloride, at the temperatures of their boiling points, extract iodine from the "hypoiodite" only very slowly. Water decomposes it, slowly at the ordinary temperature and rapidly on boiling, with formation of magnesium iodide and iodate. Quantitative experiments were made, to determine the relation between the amount of iodine absorbed by the magnesia and the concentration of the iodine solution in which the absorption occurred. With aqueous potassium iodide as solvent, no definite results could be obtained, owing to the disturbing effect of the chemical action of the water. In anhydrous chloroform, the amount absorbed diminished with the final concentration of the solution, but much less rapidly than this. The authors consider that the formation of the "hypoiodite" is analogous to cases of absorption, such as that of acids by silk, or of iodine by starch (compare Walker and Appleyard, Trans., 1896, 1334; Küster, Abstr., 1895, i, 199). J. W.

**Action of Cuprous Oxide on Silver Nitrate Solutions.** By PAUL SABATIER (*Compt. rend.*, 1897, **124**, 363—366).—When cuprous oxide is treated with successive quantities of silver nitrate solution, until no more copper is dissolved, and the residue is washed with cold water and dried by exposure to air, the product is a greenish-grey powder consisting of a mixture of basic copper nitrate and metallic silver, part of the latter being filiform; it has the composition, $Ag_6 + Cu(NO_3)_2,3CuO,3H_2O$, one-third of the nitric acid of the silver nitrate being found in the precipitate. If the silver nitrate solution is hot, the product is practically the same.

The grey mixture is insoluble in cold water, but when treated with boiling water, some cupric nitrate is dissolved, but the solution contains no nitrite. Nitric acid dissolves it readily and completely; concentrated sulphuric acid attacks it violently, with the formation of copper nitrosodisulphonate (Abstr., 1896, ii, 599, 622, 641) in consequence of the reducing action of the metallic silver on the sulphuric acid and

liberated nitric acid; dilute sulphuric acid dissolves all the copper and part of the silver; acetic acid behaves similarly, but dissolves very little silver; hydrochloric acid dissolves all the copper, and leaves a residue of violet-coloured, silver chloride. C. H. B.

**Silicides of Copper and Iron.** By GUILLAME J. L. DE CHALMOT (*Amer. Chem. J.*, 1897, **19**, 118—123).—The author finds that the crystalline copper silicide of the composition $Cu_2Si_3$ previously described by him (Abstr., 1896, ii, 362) is not a true chemical compound, but a mixture of silicon, copper silicide, and copper, the copper silicide present never containing more silicon than is represented by the formula $Cu_2Si$. In the case of a silicide containing excess of silicon, there is less silicon united with copper than would be the case if the latter were present only in the form of $Cu_2Si$. In order to prove whether a part of the copper is present as a silicide containing less silicon or in the free condition, some of the crystals were triturated with mercury in a mortar. After filtering through linen and evaporating the mercury, a residue of cuprous oxide was left. Evidently, therefore, free copper, free silicon, and copper silicide can exist side by side in the electric furnace.

A silicide of iron having the composition $FeSi_2$ is also described, obtained in grey, metallic crystals by treatment with small quantities of hydrofluoric acid of an iron-silicon alloy containing about 39 per cent. of silicon. A. W. C.

**Action of Carbonic Anhydride and Carbonic Oxide on Aluminium.** By ANTOINE GUNTZ and ARTHUR MASSON (*Compt. rend.*, 1897, **124**, 187—190).—It is known that aluminium becomes incandescent when heated in a mixture of carbonic anhydride and iodine vapour, and this is generally attributed to the combination of the halogen with the metal. The authors find, however, that a considerable absorption of carbonic anhydride takes place, and that the incandescence is more intense if carbonic oxide is substituted for the anhydride, but does not take place at all in a mixture of iodine vapour and hydrogen. When heated in carbonic anhydride only, finely-powdered aluminium is, as a rule, only slightly affected, but the commercial powder often becomes incandescent, and the product evolves considerable quantities of methane when treated with water. If the aluminium is heated to dull redness in carbonic oxide or anhydride containing a small quantity of the vapour of aluminium chloride or iodide, the metal readily becomes incandescent, and is more or less completely converted into the carbide $Al_4C_3$ which yields methane on treatment with water. C. H. B.

**Action of Nitrogen Oxides on Ferrous Chloride and Bromide.** By VICTOR THOMAS (*Compt. rend.*, 1897, **124**, 366—368).—Ferric bromide is reduced more readily than the chloride by nitric oxide with formation of ferrous bromide and nitrosyl bromide, and the ferrous bromide absorbs nitric oxide; but whether the compound has the composition $5Fe_2Br_4,NO$ or $6Fe_2Br_4,NO$ has not yet been definitely ascertained. It does not alter in dry air, nor does it lose nitric oxide in a vacuum. Ferrous bromide in solution absorbs nitric oxide in the same way as other ferrous salts, but the compound

formed has not yet been isolated, although it seems to be crystallisable.

Ferrous chloride or bromide readily absorbs dry nitric peroxide, the compound formed being $2Fe_2Cl_4,NO_2$, or $2Fe_2Br_4,NO_2$. Both compounds are stable when exposed to air, and do not lose nitrogen peroxide in a vacuum. In most reactions, however, they split up into a mixture of ferrous salt and nitrogen peroxide. When dissolved in water, for example, alkalis precipitate black iron oxide from the solution.

In presence of moisture, the two ferrous salts seem to absorb even larger quantities of nitric peroxide, but the reaction is complicated, and some chlorine (or bromine) is removed. C. H. B.

**Organic Compounds which prevent the Precipitation of the Hydroxides of Iron, Nickel, and Cobalt.** By JAN ROSZKOWSKI (*Zeit. anorg. Chem.*, 1897, **14**, 1—20).—Of 111 organic compounds which were examined, only 25 prevent precipitation of the hydroxides of these metals, and these compounds belong to the polyacid alcohols, the carbohydrates, the hydroxy-monobasic or polybasic acids, and in a few cases to the amido-acids, the poly-acid phenols, and the phenolic acids. The monobasic and polybasic organic acids prevent the formation of the hydroxides only in acid or neutral solutions; in alkaline solutions, a precipitate is nearly always obtained, although it is often some time in forming. Most of the organic compounds which prevent the formation of the hydroxides belong to the fatty series, and the corresponding aromatic compounds, with a few exceptions, are without influence. These, also, all contain the hydroxyl group, and if this group is replaced by another monatomic basic or acid group, the compounds formed are without influence, except in the case of the amido-compounds, which form soluble complex salts with copper and nickel.

These organic compounds have a very varying influence on the precipitation of the hydroxides. Of 25 compounds, 22 prevented the precipitation of hydroxide from a solution of ferric chloride; and only 9 prevented the precipitation of hydroxide from ferrous sulphate. The capability of forming complex soluble compounds increases with the number of the hydroxyl groups; the monhydric alcohols are without influence on the precipitation; but, commencing with glycol, the influence is proportional to the number of the hydroxyl groups.

E. C. R.

**Nomenclature of Ammonio-cobalt Compounds.** By ALFRED WERNER (*Zeit. anorg. Chem.*, 1897, **14**, 21—27).—Those atoms, or groups of atoms, which form with the metal a complex radicle, are placed before the name of the metal in the following order: first, the name of the acid-residue, then the groups similar to the ammonia group, and immediately preceding the name of the metal the ammonia (ammino) groups. The ammonia group is designated by the word *ammine*, to distinguish it from the *amine* of organic compounds. All other groups and atoms which do not belong to the complex radicle are placed after the name of the metal. In the case of isomeric compounds, the author numbers the groups comprised in the complex with the angles of the octahedron which they occupy in relation to the metallic atom in accordance with his theory.

Those names which refer to the colour of the compounds are not employed. A few examples are given below.

| New name. | Formula. | Old name. |
|---|---|---|
| Hexamminocobalt salts | $[Co(NH_3)_6]X_3$ | Luteocobalt salts. |
| Aquopentamminocobalt salts .................. | $[Co(NH_3)_5OH_2]X_3$ | Roseocobalt salts. |
| Nitritopentamminocobalt salts ............ | $[Co(NH_3)_5NO_2]X_2$ | Xanthocobalt salts |
| 1 : 6-Dichlorotetramminocobalt salts ......... | $[Co(NH_3)_4Cl_2]X$ | Dichloropraseo-cobalt salts. |
| 1 : 2 : 4-Trinitritotriammine cobalt ......... | $Co(NH_3)_3(NO_2)_3$ | [(Gibbs'). Triaminecobalt nitrite |
| 1 : 2 - Dinitritotetramminocobalt salts ... | $[Co(NH_3)_4(NO_2)_2]X$ | Flavocobalt salts. |

E. C. R.

**1 : 6-Dichlorotetramminocobalt Salts (Chloropraseo-salts).** By ALFRED WERNER and ARNOLD KLEIN (*Zeit. anorg. Chem.*, 1897, **14**, 28—41).—*Dichlorotetramminocobalt hydrogen sulphate* $(Co(NH_3)_4Cl_2)\cdot SO_4H$, is prepared by treating the solid carbonatotetrammine chloride, $Co(NH_3)_4CO_3Cl$, with concentrated hydrochloric acid in a freezing mixture, dissolving the product in concentrated sulphuric acid, and adding hydrochloric acid as long as a precipitate is formed; the mixture is then allowed to remain for a few days in a closed flask, and the precipitate collected and washed with alcohol and ether; it is easily purified by dissolving it in water and precipitating with dilute sulphuric acid. It crystallises in beautiful, dark green needles, is easily soluble in water, and has a strongly acid reaction. With hydrochloric acid and chlorides, it yields a bright green, crystalline precipitate of dichlorotetramminocobalt chloride; it is decomposed by mercurous nitrate, potassium cyanide, and potassium ferrocyanide, and dissolves in concentrated sulphuric acid with a red coloration and evolution of hydrogen chloride. It is more stable in aqueous solution than the other salts of the series, but the colour of the solution gradually changes to blue, violet, becomes colourless, and finally red. When the concentrated aqueous solution is warmed, a precipitate of chloraquotetramminocobalt sulphate, $[Co(NH_3)_4ClH_2O]SO_4$, is obtained in the form of lustrous, reddish-violet plates; this dissolves in concentrated sulphuric acid with a violet coloration, and when treated with concentrated hydrochloric acid in aqueous solution, yields chloraquotetramminocobalt chloride. The *silver* salt, $[Co(NH_3)_4Cl_2]SO_4Ag$, is obtained as a flocculent, bright green precipitate by mixing solutions of equivalent quantities of the hydrogen sulphate and silver nitrate at a low temperature. The *bismuth* salt, $Bi[Co(NH_3)_4Cl_2SO_4]_3$, is obtained in a similar way as a green, pulverulent precipitate. The *chloride*, $[Co(NH_3)_4Cl_2]Cl$, *bromide, iodide, fluoride, nitrate, nitrite, thiocyanate, platinochloride, platinosochloride, aurochloride, dichromate, chromicyanide,* and *ferricyanide* are also described. With mercuric chloride, potassium- and dipotassium-mercuric chloride, varying mixtures of salts are obtained according to the conditions, but the authors were unable to isolate a pure salt.

A cobalt ammonium sulphite compound is described by Vortmann and Magdeburg (Abstr., 1890, 14), which, according to its method of pre-

paration, should belong to the 1 : 6-dichlorotetrammine salts; the authors have repeated this experiment, and obtained a compound which is not a dichlorotetrammine salt. They are engaged in further investigations.

E. C. R.

**Chromium and Manganese Phosphides.** By A. GRANGER (*Compt. rend.*, 1897, **124**, 190—191).—Chromic chloride is reduced to chromous chloride when heated with phosphorus in presence of carbonic anhydride, but no phosphide is formed. Manganous chloride can be volatilised in phosphorus vapour without any decomposition taking place. If, however, the carbonic anhydride is replaced by hydrogen, *chromous phosphide*, CrP, and *manganous phosphide*, $Mn_3P_2$, are formed respectively, a result probably due to an intermediate formation of hydrogen phosphide.

Chromous phosphide is a grey solid with a graphitoidal appearance; it is not affected by aqua regia. Manganous phosphide forms highly lustrous, slender needles, and is attacked by aqua regia. Neither compound is affected by nitric acid, but both are readily attacked by chlorine, with incandescence, and both are slowly oxidised when heated in air. They are also decomposed by fused potassium hydroxide.

C. H. B.

## Mineralogical Chemistry.

**Molybdenum, Selenium, &c., in Coal from Liége.** By ARMAND JORISSEN (*Ann. Soc. Geol. Belgique*, 1896, **23**, 101—105).—The brownish-grey flue-dust, produced when Liége coal is burnt, contains ammonium salts, sulphates, and iron; and in the aqua regia extract, traces of the following were found, Se, Mo, Sb, Bi, Ni, Co, As, Cu, Pb, Zn, Ca. L. J. S.

**Artificial Antimonite [Stibnite] and Bismuth Crystals.** By P. PHILIPP HEBERDEY (*Ber. Akad. Wien*, 1895, **104**, i, 254—266).—Crystals of stibnite are described from a specimen of slag from the smelting works of Przibram in Bohemia; they attain a length of 1 cm., and are found in drusy cavities in a material which is shown by analysis to be mainly a mixture of $Fe_2S$ and $Cu_2Sb$. Other layers of this specimen are shown by analysis to consist of mixtures of metasilicates and sulphides.

Acicular crystals of bismuth from another furnace product from Przibram are of unusual habit; they consist of elongated hexagonal prisms, $b\{2\bar{1}\bar{1}\}$, with irregular terminations showing the forms $o\{111\}$, $e\{011\}$, $s\{\bar{1}11\}$. There is a perfect cleavage parallel to $b$, a good one parallel to $o$, and others, less distinct, parallel to $e$ and $s$. L. J. S.

**A Tellurium Mineral from Colorado.** By RICHARD PEARCE (*Proc. Colorado Sci. Soc.*, 1896, [Oct. 5th], pp. 2).—A dark grey mineral, with bright, metallic lustre, from the Griffith mine, near Georgetown, was freed as far as possible from intermixed pyrites, galena, copper pyrites, and magnesite, and analysed by F. C. Knight; it gave

| Ag. | Te. | Pb. | Cu. | Fe. | Bi. | S. | $MgCO_3$. | Au, Ag. | Insol. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|
| 50·65 | 18·80 | 9·34 | 4·65 | 4·00 | 1·16 | 8·06 | 1·95 | 0·48 | 1·07 | 100·16 |

After deducting impurities, this corresponds with a mixture of two parts of hessite ($Ag_2Te$) and one of argentite ($Ag_2S$). The gold exists as an alloy with silver. L. J. S.

[Bismutosmaltine, Wolframite, Agricolite, &c.] By AUGUST FRENZEL (*Tscher. Min. Mitth.*, 1897, **16**, 523—529).—The bismuth veins of Zschorlau, Schneeberg, Saxony, carry native bismuth, bismuthic ochre, several uranium minerals, and the following new mineral, to which the name *bismutosmaltine* is given. The last was found in a large nodule of dark blue-grey ore which assayed 40·5 per cent. Bi, and 6·6 Cu; the small cubic crystals are apparently holohedral with the forms $a\{100\}$, $o\{111\}$, $d\{110\}$; the colour is tin-white; strong metallic lustre; streak-black; brittle; H = 6, sp. gr. 6·92. Analysis of pure hexahedral crystals, free from native bismuth, gave

| Bi. | Cu. | As. | Sb | Co. | Fe. | S. | Total. |
|---|---|---|---|---|---|---|---|
| 20·17 | 0·69 | 61·59 | 0·16 | 13·70 | 3·71 | 0·05 | 100·07 |

The copper and sulphur are due to the presence of copper pyrites, deducting these, $Bi + As + Sb : Co + Fe = 3·07 : 1$, giving the formula $Co(As,Bi)_3$. This is like skutterudite, but with some arsenic replaced by bismuth; the tin-white colour of the mineral is more like the colour of smaltite than that of skutterudite. Cheleutite ("wismuthkobalterz") is related to this, although it is usually considered as a variety of smaltite containing native bismuth.

Wolframite crystals are described from Uncia (prov. Chayanta), Oruro, and Chorolque, in Bolivia. The habit varies considerably; sometimes, by the development of the three axial planes, the crystals have a cubic appearance. Bismuth minerals occur on the specimens. Analysis of material from Uncia, of sp. gr. 6·96, gave

| $WO_3$. | $SnO_2$. | FeO. | MnO. | Insol. | Total. |
|---|---|---|---|---|---|
| 73·42 | — | 18·57 | 6·64 | 1·16 | 99·79 |
| 71·68 | 0·65 | 19·68 | 6·20 | 1·70 | 99·91 |

Agricolite is described from a new locality, namely Schwarzenberg, Saxony; it here occurs on bismuthic ochre as radial aggregates, of a greyish yellow or green colour, and resembles wavellite. An oblique extinction of 51° was observed; and besides bismuth silicate, traces of phosphoric acid were found.

Copper glance from the Freiberg district is mentioned as containing 2 per cent. of silver. Pseudomorphs of copper glance after mispickel and of stilpnosiderite after uranite are described. Arsenic rhombohedra are described from Nagyag and Japan; the sp. gr. of the latter is 5·70. L. J. S.

The so-called Dicksbergite. By MATS WEIBULL and AUG. UPMARK (*Geol. För. i Stockholm Förh.*, 1896, **18**, 523—526).—A mineral from Dicksberg, parish of Ransäter, Wermland, recently described by L. J. IGELSTRÖM (*Geol. För. Förh.*, 1896, **18**, 231) as a new mineral, under the name of dicksbergite, crystallising in the orthorhombic system and containing titanic acid, thorium, iron, cerium, didymium, yttrium, tin, and tungsten, is here shown to be merely rutile. Besides 98·13 per cent. $TiO_2$, iron alone is present; the sp. gr.

of 4·20, and the optical and crystallographic characters agree with those of rutile. L. J. S.

**Monazite.** By H. B. C. NITZE (*16th Ann. Rept. U.S. Geol. Survey for* 1894—5, 1895, part iv, 667—693).—This is a monograph of the mineral, and gives a summary of the history, and of the crystallographic, physical, and chemical characters; the known localities are enumerated, and a bibliography is added; the uses and methods of extraction are also described. Thirty-seven analyses are quoted. Monazite sand, containing up to about 67 per cent. of monazite, from North Carolina, contains, according to analyses by C. Baskerville, 0·125 to 6·54 per cent. of thoria. L. J. S.

**[Mispickel, Vivianite, &c., from Bohemia.]** By FRIEDRICH KATZER (*Tscher. Min. Mitth.*, 1897, 16, 504—518).—Massive, granular mispickel from a deposit in decomposed red granite near Sestroun̆, north-east of Selčan, gave the following results on analysis; II was made in the k.k. geol. Reichsanstalt.

| | S. | As. | Fe. | Au. | Ag. | Total. | Sp. gr. |
|---|---|---|---|---|---|---|---|
| I. | 19·96 | 45·53 | 33·66 | trace | nil | 99·15 | 6·179 |
| II. | — | 34·40 | — | 0·0012 | 0·0014 | — | — |

Vivianite occurs in pegmatite at Kloub, near Protiwin, as earthy crusts of a sky-blue colour; it is at first almost white (sp. gr. 2·658), but, on exposure, soon becomes greenish, and finally blue. In larger cavities, there are good crystals (sp. gr. 2·587) of a light greyish-green colour, but they become blue on exposure to air. The percentages of water found in the earthy variety, arranged according to the intensity of the blue colour and commencing with the lightest, were 27·33, 27·65, 27·12, 28·12, 28·66, mean 27·77; this indicates that the change in colour is connected with the absorption of water from the air. Crystals gave, 27·08, 26·68 and 26·99, mean 26·92, per cent. of water, and 3·08 $Fe_2O_3$, 41·12 FeO per cent. As regards the origin of the vivianite, it could have been derived from the apatite in the pegmatite, or have been deposited by infiltering organic matter; the latter is the more probable.

Crystals of mimetite are described from Hodowitz; sp. gr. 7·126; 75·12 per cent. Pb. Descriptions are also given of crystals of calcite; of an occurrence of anthracite with quartz in porphyry; and of an occurrence in sandstone of viscous petroleum of sp. gr. 0·92. L. J. S.

**Munkforssite, Bliabergite and Ransätite, Three New Swedish Minerals.** By LARS J. IGELSTRÖM (*Zeit. Kryst. Min.*, 1897, 27, 601—604)—In the gneiss of the parish of Ransäter, in Wermland, are thick bands of quartz, which is quarried at Bliaberg and Dicksberg for the preparation of a refractory material for the iron furnaces of Munkforss. In the white quartz are plates of damourite, bands of pyrites, also apatite, zircon, kyanite, ilmenite, and the three new minerals described below.

*Munkforssite* occurs in kyanite at Dicksberg; it is white, then resembling quartz, or sometimes pale reddish, and is transparent to translucent. It occurs as grains, and as "monosymmetric" crystals. It is infusible, and is only partially decomposed by acids. In the closed tube, it gives only a trace of acid water. The results of the

analysis are given under I; deducting the undecomposed portion (damourite), and adding the loss on ignition to the $SO_3$, the composition of the mineral is given under II.

| | $SO_3$. | $P_2O_5$. | $Al_2O_3$. | CaO. | FeO. | Cl. | Loss on ignition. | Insol. | Total. |
|---|---|---|---|---|---|---|---|---|---|
| I. | 13·20 | 13·98 | 25·54 | 32·00 | trace | trace | 2·63 | 10·74 | 98·09 |
| II. | 18·12 | 16·01 | 29·23 | 36·64 | — | — | — | — | 100·00 |

This somewhat resembles the rhombohedral svanbergite in composition. The pale green *kyanite*, which contains the munkforssite, gave $SiO_2$, 43·91; $Al_2O_3$, 56·52; FeO, trace = 100·43 per cent.

*Bliabergite* (spelt bliabergsite in *Geol. För. Förh.*, 1896, **18**, 41).—This occurs plentifully in the white damourite of Bliaberg as "rhombohedral" crystals, which when fresh are almost black (anal. I), but when weathered are more or less red (anal. II). H = 4·5. It is infusible, and is only partially decomposed by acids.

| | $SiO_2$. | $Al_2O_3$. | FeO. | MnO. | MgO,CaO. | $Fe_2O_3(Mn_2O_3)$ | $H_2O$. | Total. |
|---|---|---|---|---|---|---|---|---|
| I. | 39·13 | 27·60 | 26·74 | 4·45 | 0·43 | — | 3·26 | 101·61 |
| II. | 41·67 | 23·81 | — | — | — | 27·38 | 7·14 | 100·00 |

From I is deduced the formula $2(Fe,Mn)_2SiO_4 + Al_4Si_3O_{12}$, or $3(Fe,Mn)_2SiO_4 + 2Al_2SiO_5$; and from II, $Al_4Si_3O_{12} + 2H_2O$. [M. Weibull (*Geol. För. Förh.*, 1896, **18**, 515) shows this to be near ottrelite].

*Ransätite* (*Geol. För. Förh.*, 1896, **18**, 43), also from the damourite of Bliaberg, occurs as pale red, globular masses. The crystal system is given as cubic. H = 6. Before the blow-pipe, it becomes black and is infusible; insoluble in acids. Analysis gave

| $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$. | MnO. | CaO. | MgO. | Total. |
|---|---|---|---|---|---|---|
| 43·47 | 14·50 | 17·72 | 14·97 | 5·63 | 2·57 | 98·86 |

The formula is given as $3(Mn,Ca,Mg)SiO_3 + (Fe,Al)_4Si_3O_{12}$.

L. J. S.

**Artificial Gypsum.** By L. Jowa (*Ann. Soc. Geol. Belgique*, 1896, **23**, pp. cxxviii—cxxx).—Cesàro has previously obtained small crystals of gypsum by allowing a solution of ferrous sulphate, in contact with the air, to act on chalk. The present author has kept the same materials for four months in a long necked flask; by retarding the rate of oxidation of the ferrous sulphate in this way, good crystals have been obtained. The pieces of chalk become coated with ferric hydroxide and acicular gypsum crystals. The crystals show the forms *b* {010}, *m* {110}, *l* {111}; the largest, 1 cm. long, are elongated in the direction of the vertical axis, but others are elongated in the direction of the edge [111, $1\bar{1}1$]. Twin crystals, with *a*(100) the twin plane, are also present. L. J. S.

**Leonite from Leopoldshall.** By C. August Tenne (*Zeit. deut. geol. Ges.*, 1896, **48**, 632—637).—The artificial salt, $MgSO_4,K_2SO_4 + 4H_2O$, has been prepared artificially by van der Heide (Abstr., 1893, ii, 276) who named it potassium-astrakanite; and the natural mineral from Westeregeln, where it has been known at the salt works since 1889, has been described by Naupert and Wense (Abstr., 1893, ii, 325), and analysed by Geserich, who found

| $K_2SO_4$. | $MgSO_4$. | $Na_2SO_4$. | NaCl. | $MgCl_2$. | $H_2O$. |
|---|---|---|---|---|---|
| 40·2—45·3 | 32·0—34·3 | 1·3 | 0·5—3·5 | 0·3—4·8 | 19·3—20·7 |

As shown in the present paper, there is no crystallographic relation between this mineral and blödite (=astrakanite, $MgSO_4,Na_2SO_4+4H_2O$), so that the older but unpublished name, leonite, is used in preference to kaliblödite or kaliastrakanite. At Leopoldshall, near Stassfurt, the mineral occurs as thick, tabular crystals, along with kainite and rock salt; the colour is faintly yellowish, but sometimes reddish, greyish, or bright canary yellow. Between these large, indistinct crystals are kieserite and thin, colourless, monosymmetric crystals of leonite, tabular parallel to c{001} and with many small planes at the edges; $a:b:c = 1·03815:1:1·23349$; $\beta = 84° 50'$. The optic axial plane is perpendicular to the plane of symmetry, and makes an angle of $29\frac{1}{2}°$ with the base. There is no distinct cleavage; fracture conchoidal. It is soluble in water; analysis by Braun gave

| Mg. | K. | $SO_4$. | Cl. | $H_2O$. | Insol. | Na. | Total. |
|---|---|---|---|---|---|---|---|
| 6·54 | 25·48 | 43·73 | 4·84 | 18·99 | 0·42 | nil | 100·00 |

Deducting 10·16 per cent. of KCl as impurity, this gives $MgSO_4,K_2SO_4+4H_2O$. The small, colourless crystals contained no chlorine.

L. J. S.

**Wolframite from Argentina.** By GUILLERMO BODENBENDER (*Zeit. Kryst. Min.*, 1896, **27**, 533—534; from *Zeit. prakt. Geol.*, 1894, 409—414).—Wolframite occurs with apatite, copper pyrites, molybdenite, fluorite, scheelite, mica, and chlorite in granite, and in the quartz veins of the neighbouring gneiss near to Sauce, Dept. Calamuchita, not far from the crest of the Sierra de Córdoba. Analysis of the wolframite gave

| $WO_3$. | $Nb_2O_5$. | FeO. | MnO. | Total. |
|---|---|---|---|---|
| 74·86 | 1·22 | 13·45 | 11·02 | 100·55 |

Here Fe : Mn = 4 : 3. L. J. S.

**Meerschaum from Eskishehir, Asia Minor.** By ERNST WEINSCHENK (*Zeit. Kryst. Min.*, 1897, **27**, 574—576).—The composition of meerschaum is somewhat uncertain, as different analyses show varying amounts of water. The material from Eskishehir, examined by the author, is seen under the microscope to be a compact, fibrous aggregate with weak birefringence. The air-dried material loses 14·35 per cent. over sulphuric acid, at 210° there is a further loss of 0·88 per cent., and up to 300° there is no more loss; material which has been heated up to 300° retains its original optical character, so that the water lost below this temperature must be considered to be hygroscopic, and contained in the fine pores of the mineral. The water directly determined on material dried at 210° amounted to 12·10 per cent.; this corresponds with the formula $H_4Mg_2Si_3O_{10}$. In Asia Minor, meerschaum occurs associated with magnesite veins in serpentine, but it has probably not been derived from the magnesite. L. J. S.

**[Halotrichite, Dioptase, and Rhodochrosite from Argentina.]** By GUILLERMO BODENBENDER (*Bol. Acad. Cien. Córdoba*, 1894, **14**, 110—115).—The shores of a lake on the slopes of the volcano of Copahué are coated with an efflorescence of a white, porous material having a granular or fibrous structure, with delicate needles in places (I); another sample is pulverulent and without needles (II). Sulphur occurs mixed with the salts, this being deposited from the hot water

of the lake, which is charged with hydrogen sulphide. Lemon-yellow coquimbite is also present.

| | $SO_4$. | $Al_2O_3$. | $Fe_2O_3$. | CaO. | MgO. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|---|
| I. | 41·203 | 12·234 | 6·639 | trace | trace | 40·010 | 100·086 |
| II. | 35·509 | 13·012 | 0·681 | 0·674 | 0·236 | [49·888] | 100·000 |

The iron is partly as FeO, and one determination gave 1·098 per cent. FeO. The composition of the deposit is variable, and, as seen from the analyses, differs somewhat from that of halotrichite.

Dioptase occurs in a quartz vein in gneiss in the Sierra Chica, Córdoba, as prismatic crystals with rhombohedral terminations, the largest measuring 12 × 5 mm.; more often it occurs as a thin incrustation, or filling fissures; it is associated with linarite, malachite, azurite, cerussite, and chrysocolla. As crystals were plentiful, the following analysis was made.

| $SiO_2$. | CuO. | $Fe_2O_3$. | $H_2O$ [diff.]. |
|---|---|---|---|
| 38·384 | 50·674 | 0·674 | [10·266] |

Rhodochrosite, which occurs with galena, blende, and barytes at Capillitas in Catamarca, varies considerably in colour, texture, and composition. It is usually concretionary, but is sometimes found as small rhombohedra of a reddish colour; analysis II was made on material showing some crystals.

| | $MnCO_3$. | $CaCO_3$. | $FeCO_3$. | $MgCO_3$. | Total. |
|---|---|---|---|---|---|
| I. | 90·099 | 3·913 | 3·614 | 2·451 | 100·077 |
| II. | 93·064 | 2·658 | 2·843 | 2·106 | 100·671 |

A greyish-white compact specimen contained only 62 per cent. $MnCO_3$. Vivianite from Córdoba is also described. L. J. S.

**Mineral Veins in the Serpentines of the Austrian Alps.** By Ernst Weinschenk (*Zeit. Kryst. Min.*, 1897, **27**, 559—573).—It is pointed out that in the mineral veins which occur in connection with the serpentines of the East Central Alps (this vol., ii, 106), magnesium minerals are of somewhat exceptional occurrence; in the present paper, occurrences of olivine and serpentine in veins in the stubachite (*Abhand. k. bayer. Akad. Wiss.*, II Cl., 1894, **18**, 653) of the Stubachthal are described. The olivine, when it is embedded in calcite, is present as good crystals; analysis by Vötter gave

| $SiO_2$. | FeO. | MgO. | $TiO_2$. | Total. | Sp. gr. |
|---|---|---|---|---|---|
| 39·69 | 12·43 | 48·33 | nil | 100·45 | 3·357 |

The optic axial angle is very near to 90°.

In calcite veins, in the serpentine of Scheidmoosgraben near Bruck, are radial aggregates of aragonite which somewhat resembles hydromagnesite in appearance; analysis gave

| CaO. | MgO. | Loss on ignition. | $H_2O$. | Sp. gr. |
|---|---|---|---|---|
| 55·68 | 0·20 | 43·82 | 1·00—1·29 | 2·900 |

In connection with this, the aragonite and hydromagnesite of Texas, Pennsylvania, were examined. L. J. S.

**Augite Crystals from the Central Plateau [of France].** By Ferdinand Gonnard (*Zeit. Kryst. Min.*, 1897, **27**, 614; from *Bull. soc. fran. min.*, 1895, **18**, 99—105).—Augite crystals from various

localities are described. Isolated, simple, and twinned crystals of the usual combination, from the lapilli-tufts of Puy de la Rodde, Puy-de-Dôme, gave, on analysis by Pisani,

| $SiO_2$. | CaO. | MgO. | FeO. | $Al_2O_3$. | $K_2O,Na_2O$. | Loss on ignition. | Total. | Sp. gr. |
|---|---|---|---|---|---|---|---|---|
| 47·10 | 20·25 | 12·70 | 9·60 | 10·20 | 0·84 | 0·20 | 100·89 | 3·266 |

L. J. S.

**Fuggerite, a New Mineral from the Fassathal.** By Ernst Weinschenk (*Zeit. Kryst. Min.*, 1897, **27**, 577—582).—This occurs with calcite in a hornfels close to the monzonite contact. The fresh, apple-green crystals are thick, tetragonal tables, and closely resemble gehlenite in appearance, but have a perfect basal cleavage, and are slightly harder and denser than the latter mineral. It is very easily decomposed, with separation of pulverulent silica, by dilute hydrochloric or organic acids, or even on long standing in distilled water. The specific gravity of the crystals, which, however, contain a little calcite, is 3·175—3·180. Material for analysis was separated by heavy liquids, and purified from calcite by the action of hydrochloric acid. The following results were obtained by E. Mayr.

| $SiO_2$. | $Fe_2O_3$. | $Al_2O_3$. | MgO. | CaO. | $Na_2O$. | Total. |
|---|---|---|---|---|---|---|
| 34·03 | 3·54 | 17·74 | 4·90 | 37·75 | 2·04 | 100·00 |

This agrees with a mixture of 10 molecules of gehlenite and 3 of åkermanite; but as the physical characters differ from those of Vogt's gehlenite-åkermanite group, fuggerite must be considered to belong to a dimorphous group, which is probably also tetragonal. For sodium light, fuggerite is isotropic, with a refractive index of 1·691, and for other colours the double refraction is exceedingly small; sections perpendicular to the base show a dark blue tint between crossed nicols.

L. J. S.

**Manganandalusite from Vestanå.** By Helge Bäckström (*Geol. För. i Stockholm Förh.*, 1896, **18**, 386—389).—This new variety of andalusite is of wide distribution in the quartz-muscovite- and kyanite-schists in the neighbourhood of Vestanå, N.E. Scania. It occurs as grains of a grass-green colour, and only differs from ordinary andalusite in the high content of manganese and in the remarkable strength of the pleochroism; even in thin rock sections, the pleochroism is very marked, with $a = \mathfrak{c}$ and $b = \mathfrak{b}$ blue-green, and $c = \mathfrak{a}$ intense pure yellow. Analysis by H. Santesson gave

| $SiO_2$. | $Al_2O_3$. | $Mn_2O_3$. | CaO. | $Fe_2O_3$. | Total. |
|---|---|---|---|---|---|
| 36·72 | 56·99 | 6·91 | trace | nil | 100·62 |

This agrees with the formula $(Al,Mn)_2SiO_5$. The largest amount of manganese previously found is 0·83 per cent. $Mn_2O_3$, this being in andalusite from Lisens Alp, Tyrol, analysed by Erdmann. The green andalusite of Brazil contains no manganese, and is not so pleochroic as the mineral here described.

L. J. S.

**Clay.** By Heinrich Ries (16*th Ann. Rept. U.S. Geol. Survey, for* 1894—5, 1895, part iv, 523—575).—In this paper, which is on the technology of the clay industry, 450 analyses of kaolin and various kinds of clays are given or quoted.

L. J. S.

**Meteoric Iron from Locust Grove, North Carolina.** By EMIL W. COHEN (*Ber. Akad. Berlin,* 1897, 76—81).—This iron, weighing $10\frac{1}{3}$ kilos. was found on July 29, 1857, at Locust Grove, Henry Co., and had been kept at a house in Georgia until 1895. A bright meteor was seen in the locality on June 26, 1857, but the very thin coating of rust on the surface of the iron is probably more than would have been formed in three days. The structure is granular, with an absence of octahedral and twin lamellæ; the etched surfaces of the grains show numerous minute, rounded elevations. In the outer portion of the meteorite, nodules of graphite and troilite and a platy phosphide of iron and nickel are present, whilst in the central portion there is rhabdite. Analysis by O. Sjöström gave,

| Fe. | Ni. | Co. | Cu. | C. | S. | P. | Cl. | Total. | Sp. gr. |
|---|---|---|---|---|---|---|---|---|---|
| 94·30 | 5·57 | 0·64 | trace | 0·02 | 0·05 | 0·18 | 0·01 | 100·77 | 7·7083 |

This corresponds with the following mineralogical composition,

| Kamacite. | $Fe_2NiP$. | Troilite. | Lawrencite. |
|---|---|---|---|
| 98·70 | 1·16 | 0·12 | 0·02 |

L. J. S.

**Stony Constituents of the Meteoric Iron of Toluca, Mexico.** By E. A. HUGO LASPEYRES (*Zeit. Kryst. Min.*, 1897, **27**, 586—600).—A microscopical examination of this iron (*Zeit. Kryst. Min.*, 1895, **24**, 485) has pointed to the probable presence of zircon, quartz, plagioclase, orthoclase, garnet, augite, olivine and apatite. To obtain chemical proofs of the presence of these, 585 grams of the rust was treated with hydrochloric acid, &c.; there then remained an insoluble residue weighing 1·6100 gram, of this, 0·00125 was insoluble in a mixture of hydrofluoric and sulphuric acids, the remainder consisting, as calculated from the analysis, of

| Orthoclase. | Plagioclase. | Augite. | Quartz. | Total. |
|---|---|---|---|---|
| 2·45 | 25·26 | 37·40 | 34·89 | 100·00 |

Traces of copper, tin, nickel, cobalt, and titanium were also found in the hydrofluoric acid solution. The insoluble portion consisted of cosmochlore, well-developed crystals most probably of zircon, chromite, and some undetermined splinters.

*Cosmochlore* (kosmochlor) is the name given to small, emerald-green crystals which are probably monosymmetric; the angle of optical extinction on the perfect cleavage parallel to the plane of symmetry makes an angle of 12° 14′ with the trace of a good cleavage which is perpendicular to the last; the substance is strongly pleochroic; it is infusible, and has a sp. gr. greater than 3·158. The result of an analysis on 0·0033 gram is given as:

| $SiO_2$. | $Al_2O_3$. | $Cr_2O_3$. | $Fe_2O_3$. | CaO. | MgO. | Total. |
|---|---|---|---|---|---|---|
| 31·82 | 9·09 | 39·39 | 9·09 | 6·06 | 4·55 | 100·00 |

A formula representing a basic orthosilicate is given. To obtain 1 gram of cosmochlore, 80 kilos. of the meteorite would have to be dissolved.

L. J. S.

**Composition of the Gas Evolved from the Water of a Well near Enkhuisen.** By M. VAN BREUKELEVEEN (*Rec. Trav. Chim.*, 1896, **25**, 280—281).—The gas examined had the following composition, methane, 82·9; carbonic anhydride, 10·8; nitrogen, 6·3 per cent. by

volume. Its specific gravity = 0·6936. The gas thus agrees in composition with gases obtained from other wells in the same district (compare Oudemans, Jun., *Ann. Phys. Chem.*, **142**, 273).

J. J. S.

---

## Physiological Chemistry.

---

**Argon and Nitrogen in the Blood.** By PAUL RÉGNARD and TH. SCHLŒSING, Jun. (*Compt. rend.*, 1897, **124**, 302—304).—Blood was drawn from the jugular vein of a horse in such a manner as to avoid any contact with air, and the dissolved gases were extracted in a vacuum, passed successively over potassium hydroxide and red hot copper, and afterwards examined for nitrogen and argon. Each litre of blood was found to contain 0·42 c.c. of argon and 19·98 c.c. of nitrogen.

The authors also determined the solubility of chemical nitrogen and argon respectively at the temperature of the animal body, 38°, in water, and in the serum and blood of the horse from which carbonic anhydride had been removed as completely as possible. The results were as follows.

| | Argon. | Chemical nitrogen. |
|---|---|---|
| In 1000 c.c. of water | 25·7 c.c. | 11·3 c.c. |
| In 1000 c.c. of blood | 25·3 c.c. | 11·7 c.c. |

The results with serum were somewhat lower than those with blood. It follows that the solubility of argon and nitrogen in blood is practically the same as in water.

If the argon were simply dissolved from the air, the quantity in 1000 c.c. of blood would be 0·240 c.c., and it follows that, in the case of argon, as in the well-known case of nitrogen, the quantity actually dissolved in the blood is approximately double what it would be if simple dissolution took place. The hypothesis of the formation of an unstable compound of argon and some constituent in the blood is untenable, and this may also be said of the similar hypothesis that has been advanced in the case of nitrogen. The authors suggest that the membrane that separates the blood from the air in the lungs may be the active agent in causing the dissolution of abnormal quantities of the gases.

C. H. B.

**Estimation of Lipase.** By MAURICE HANRIOT and L. CAMUS (*Compt. rend.*, 1897, **124**, 235—237).—The activity of the lipase (this vol. ii, 149) contained in the blood of the horse (collected aseptically and preserved in sealed vessels) remains constant for many months at the ordinary temperature.

Lipase (or its fermentative activity) is best estimated by the quantity of monobutyrin that it will hydrolyse in a given time. Direct experiments show that the reaction is not influenced by the presence of sodium butyrate or glycerol in much larger quantities than could result from the reaction itself. Monobutyrin, however, has a slight influence, but this is eliminated by always using solutions of the same strength.

The activity of the lipase increases with the temperature up to about 55°, but ceases almost entirely at about 60°, and entirely at 72°. When the time of action is short, the amount of change is proportional to the quantity of serum (or lipase), but if the temperature and the time are increased this proportionality no longer holds good, and the amount of change tends towards a limit which is independent of the quantity of serum added.

The activity of the lipase may be expressed in millionths of a gram-molecule of butyric acid liberated in 20 minutes at 25°. Ten c.c. of a solution of monobutyrin (1 in 100) is mixed with 1 c.c. of the serum made neutral to phenolphthalein by means of sodium carbonate, kept at 25° for 20 minutes, and the liberated acid titrated with very dilute sodium carbonate solution, using phenolphthalein as indicator. The strength of the carbonate solution may conveniently be such that each drop neutralises 0·000001 of a gram-molecule of acid. C. H. B.

[Amount of Iron Excreted in Healthy Human Urine.] By ADOLF JOLLES (*Zeit. anal. Chem.*, 1897, **36**, 149—158. See this vol., ii, 286).

---

## Chemistry of Vegetable Physiology and Agriculture.

**Vegetable Lipase in Penicillium Glaucum.** By ERNEST GÉRARD (*Compt. rend.*, 1897, **124**, 370—371).—The ferments extracted from *penicillium glaucum* are capable of hydrolysing monobutyrin and therefore contain Hanriot's *lipase* or an analogous ferment. If the *penicillium* is cultivated on Raulin's fluid to which monobutyrin has been added, butyric acid is liberated. Emulsin, which is known to exist amongst the ferments from the *Penicillium*, does not hydrolyse monobutyrin. C. H. B.

**A Soluble Oxidising Ferment and the "Breaking" of Wines.** By PAUL CAZENEUVE (*Compt. rend.*, 1897, **124**, 406—408).—The "breaking" of wines is characterised by the rapid oxidation and precipitation of the red colouring matter on exposure to air, and it has frequently been attributed to the action of a soluble oxidising ferment, which, however, has never been isolated. If wine subject to this disease is treated with strong alcohol and the precipitate is purified by repeated reprecipitation with strong alcohol, a white substance is obtained which has all the properties of an oxydase; it may or may not be identical with laccase, and the author provisionally calls it *œnoxydase*. It acts on wine even below 0°, and is rapily destroyed at 65°, and instantaneously between 70° and 75°. With guaiacum, phenols, &c., it behaves in the same way as laccase. Sodium salicylate and calcium naphthosulphonate have little effect on the action of the ferment on wines, but sulphurous anhydride in quantities of 0·01 to 0·08 gram per litre, according to the richness of the wine in oxydase, are completely effective in checking the action of the ferment and preventing the breaking of the wine, as Bouffard found in 1894.

The author considers that the excessive quantity of œnoxydase in

the wines of Beaujolais in 1896 was due to special conditions of vegetation rather than to the presence of cryptogamic parasites.

C. H. B.

**The Formation of Mannan in Amorphophallus Konjak.** By MICHITO TSUKAMOTO (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, 2, 406—408. Compare Tsuji, Abstr., 1896, ii, 44, and Kinoshita, *ibid.*, ii, 60)—The leaves of this plant were found to contain very little starch, but in all parts of the leaves a very slimy substance (an anhydride of mannose) was observed. This, when boiled, loses its slimy character, and separates in a flocculent form; it agrees in all essential properties with Kinoshita's soluble mannan (*loc. cit.*). Neither pentosans nor galactans were found in the stalks and leaves.

In order to ascertain whether mannose, as such, is present in the stalk and blade, these were extracted with 50 per cent. alcohol, which would dissolve the sugar, but not the mannans. Only the extract from the stalk yielded any appreciable quantity of precipitate with phenylhydrazine acetate; in the case of the extract of the blade, there was a doubtful trace. The stalk seems also to contain glucose or fructose, or both.

The fact that the slimy mannan occurs in the leaf cells makes it probable that, to some extent, it has the *rôle* of starch in this plant; but it is at present impossible to say whether mannose is the first product of assimilation. The presence of mannose as such in the stalks is of great interest, as it has not before been observed in plants.

N. H. J. M.

**Physiological Observations on Lecithin.** By T. HANAI (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, 2, 503—506).—Maxwell (*Chem. Centr.*, 1891, i, 365) showed that the amount of lecithin increases during germination, and subsequently decreases. (Compare Frankfurt, Abstr., 1894, ii, 113; Loew, Abstr., 1896, ii, 55; Stoklasa, *ibid.*, ii, 266; Schulze and Steiger, *Zeits. physiol. Chem.*, 13, 386; Liebermann, *Pflüg. Arch.*, 1893; Schulze, Abstr., 1895, ii, 364.

The author's experiments were made with the leaves of *Thea chinensis* and the bark of *Prunus cerasus*. The following (I) amounts of lecithin, and (II) of ethereal and alcoholic extract (per cent. in the dry substance) were found at the different dates:

| | *Thea chinensis* (leaves). | | | | *Prunus cerasus* (bark). | | |
|---|---|---|---|---|---|---|---|
| | Old leaf. 23 Nov., 1895. | Old leaf. 26 May, 1896. | Young leaf. 1 April, 1896. | Young leaf. 26 May, 1896. | 23 Oct., 1895. | 5 April, 1896. | 9 April, 1896. |
| I. | 2·54 | 0 | 0·21 | 1·11 | 1·88 | 0·96 | 0·71 |
| II. | 26·18 | 18·19 | 9·44 | 18·67 | 10·53 | 10·97 | 9·52 |

Whilst the lecithin (and the fat) decreases in old leaves in the spring, there is a gradual increase in the young leaves. The results obtained with bark also show that lecithin is a reserve substance which is consumed in the spring (compare Kellner, Makino, and Ogasawara, Abstr., 1887, 73).

The determinations were made by Schulze's method.

N. H. J. M.

**Relative Value of Asparagine as a Nutrient for Phænogams.** By T. NAKAMURA (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, 2,

465—467).—The results of experiments in which barley and onion plants were grown in solutions of asparagine and ammonium succinate respectively showed a far greater increased growth with asparagine than with ammonium succinate. N. H. J. M.

**Relative Value of Asparagine as a Nutrient for Fungi.** By T. NAKAMURA (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, **2**, 468—470).—Spores of *Aspergillus orizæ* were suspended in water, and 1 c.c. added to each of a number of flasks containing 500 c.c. of water and (except the last) 3·06 grams of ethylic alcohol, together with different ammonium salts and asparagine respectively. After 18 days, the following amounts of fungus (dried at 100°) were obtained. The amounts of salts given and of produce are in grams.

| | Ammonium tartrate (6·33). | Ammonium malate (5·00). | Ammonium succinate (5·00). | Ammonium lactate (5·13). | Ammonium acetate (5·13). | Ammonium nitrate (2·66). | Asparagine (5.00). | (5·00). |
|---|---|---|---|---|---|---|---|---|
| Dry fungus | 0·015 | 0·011 | 0·008 | 0·006 | 0·000 | 0·002 | 0·026 | 0·016 |

The solutions contained in addition monopotassium phosphate (0·1), and magnesium sulphate (0·2 per cent.).

In a second experiment, 1 per cent. methylic alcohol was added to all the flasks (except the last), and the nitrogen compounds were added in such quantities that the ratio of nitrogen atoms to carbon atoms was as 1 : 8. The following amounts of fungus were produced in 200 c.c. of the solutions.

| Ammonium tartrate. | Ammonium chloride. | Sodium nitrate. | Urea. | Glycocine. | Asparagine (with alcohol). | Asparagine alone. |
|---|---|---|---|---|---|---|
| 0·012 | 0·025 | 0·015 | 0·028 | 0·063 | 0·073 | 0·047 |

In mycelium fungi, asparagine is more suitable as a source of nitrogen than any other of the compounds which were used, and far more so than such a nearly related compound as ammonium succinate. The same holds good also for phænogams. N. H. J. M.

**Physiological Behaviour of Maleic and Fumaric Acids.** By T. ISHIZUKA (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, **2**, 484—486).—According to Buchner (Abstr., 1892, 820), mould fungi readily utilise fumaric acid as a source of carbon, but not maleic acid, whilst Loew (*Centr. Bact.*, **12**, 361), showed that the same holds good for bacteria. Fodera (*Chem. Zeit.*, Dec., 1895) found that maleic acid is more poisonous for the higher animals, dogs, for instance, than its stereoisomeride. Very dilute solutions of the sodium salts of the two acids were without injurious action on plants; it is, however, possible that maleic acid is transformed in the plant into fumaric acid. The former is never found in plants, whilst the latter is known to occur (for instance, in *Fumaria officinalis*, *Corydalis bulbosa*, *Glaucium luteum*, in varieties of *Agaricus*, and in *Cetraria islandica*).

Young leaves of *Prunus cerasus* and *Brassica campestris* were killed in 4 and 3 days by 1 per cent. sodium maleate, in 6 and 5 days by sodium fumarate. Barley plants were killed in 20 hours in 2 per cent. maleate, but remained uninjured in the fumarate. In a number of experiments with branches, in 1 per cent. solutions of the sodium salts, the branches in every case lived longer in the fumarate than in the maleate. Similar results were obtained with seeds of barley and radish, and with filaments of *Spirogyra*.

Infusoria, rotatoria, and copepoda remained alive several days in 1

per cent. solutions, but were killed in 5 per cent. solutions—in 80 minutes in maleate, in 8 hours in the fumarate solutions.

N. H. J. M.

**Formation of Asparagine in Plants under Different Conditions.** By U. Suzuki (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, 2, 409—457).—According to Loew's theory, asparagine is a synthetical product, formed from the ammonia of the decomposed proteids (*The Energy of Living Protoplasm*, London, 1896, p. 38); and Kinoshita's experiments with two kinds of *Gramineæ* show that ammonia taken up by the roots may furnish asparagine.

The author has made over twenty sets of experiments, in which the different plants were placed in solutions of various ammonium salts, sodium nitrate, and urea, sometimes also with the addition of sugar; the experiments lasted for a week or more. The asparagine nitrogen was determined in similar plants, at the beginning of the experiments, in the plants fed with the various solutions, and in control plants kept in distilled water. Total nitrogen, and nitrogen as nitrates and as ammonia, were also determined in some cases. The plants selected were: sun-flower, yellow lupins, *Melia Japonica*, *Curcubita melo peppo*, potato plants and shoots, *Holesia hispidum*, buckwheat, varieties of *Brassica campestris*, wheat, and barley. The results point to the following conclusions.

Asparagine is derived, (1), from the decomposition of proteids and, (2), by synthesis from ammonium salts, urea, and nitrates. It is formed, not only by keeping full-grown plants in darkness, but also, under certain conditions, in full daylight. Synthetical formation is only possible in presence of sugar and, at the same time, under conditions which exclude the production of proteids. An excess of sugar prevents asparagine formation from proteids, but not its synthetical production.

Ammonia is never stored up in plants, being at once transformed into innocuous compounds, unless there is a deficiency of sugar present; in this case, a small amount remains in the plant. Direct experiments made by Aoyama showed the poisonous effect of ammonium salts when there was insufficient sugar to convert them into asparagine. Ammonium salts are generally more suitable than sodium nitrate for producing asparagine. The chloride is the best salt, whilst the phosphate is less suitable, owing probably to the stimulating action of the phosphoric acid in forming nuclein and new cells.

Urea proved, except in the case of barley, to be more suitable than ammonium salts for producing asparagine.

As regards nitrates, a high temperature and the presence of sugar are necessary for their conversion into asparagine; otherwise, they remain for some time stored up in the plant.

The conversion of asparagine into proteids is only possible when all conditions (the presence of sulphates, for instance) are fulfilled.

In etiolated shoots sodium nitrate is not converted into asparagine, whilst urea is. The addition of sugar increases the amount of asparagine formed from ammonium salts in etiolated plants. N. H. J. M.

**Can Old Leaves produce Asparagine by Starvation?** By T. Miyachi (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, 2, 458—464).—

A number of old leaves of *Pœonia albiflora* which showed incipient decay were divided into two portions, the one dried and analysed at once, the other placed in a vessel containing a little water. Microscopical examination revealed a gradual disappearance of starch granules from the mesophyll, and also a gradual decrease of the active albumin stored up in the vacuoles (*Bull.*, 224). After 14 days, the reserved leaves were analysed.

Experiments were also made with old leaves of *Thea chinensis*. The reserved leaves remained on the small branches, which were kept in the dark, in fresh water, for 24 days. The gradual disappearance of starch granules and the decrease of active albumin were again observed; soluble, passive albumin was not present at all. The following percentage amounts of nitrogen were found in the fresh and starved leaves.

| | | Total. | As Protein. | As Asparagine. | As other Amides. | As Caffeine. |
|---|---|---|---|---|---|---|
| *Pœonia albiflora* | Fresh | 1·364 | 1·312 | 0·037 | 0·015 | — |
| | Starved | 1·462 | 0·801 | 0·206 | 0·455 | — |
| *Thea chinensis* | Fresh | 3·475 | 2·850 | 0·201 | 0·141 | 0·283 |
| | Starved | 3·987 | 2·511 | 0·867 | 0·251 | 0·358 |

The results leave no doubt that even old leaves can produce asparagine from proteids.

As regards the suitability of caffeine as a source of nitrogen, a 0·5 solution infected with spores of *Aspergillus orizœ* developed only a very small amount of mycelium covered with some spores, whilst *Penicillium glaucum* failed to develop at all. In the case of tea, the experiments show that, not only is there no consumption of caffeine in starved leaves, but that the caffeine actually increased. It remains to be seen whether, in presence of much carbohydrate and absence of other source of nitrogen, caffeine can be utilised for producing proteids in tea leaves.

N. H. J. M.

**Tabasheer.** By Walter H. Ince (*Pharm. J. Trans.*, 1896, [iv], 2, 141).—Tabasheer is the name given to a white, smooth, porcelain-like substance rarely found deposited in a thin layer in the knots of the bamboo. The author's analyses of three samples show: $SiO_2$, 89·77—91·69; $Fe_2O_3$, trace—0·665; CaO, 0·725—3·81; $K_2O$, 1·524—4·332; organic matter, 0·0—3·122; water, 1·613—4·13.

R. R.

**New Kino from Myristica.** By Eduard Schaer (*Pharm. J. Trans.*, [iv], 3, 117—118).—The dried juices from the bark of several Asiatic species of *Myristica* show but little difference from officinal Malabar kino. The crude, inspissated, fresh juice from the *Myristica* species differs by containing crystalline calcium tartrate suspended in, and depositing from, it. This distinguishes it from all the other kinos of commerce.

R. R.

**Brazilian and Columbian Ipecacuanha.** By Benjamin H. Paul and Alfred J. Cownley (*Pharm. J. Trans.*, [iv], 2, 321).—By reason of the different proportions of emetine and cephæline contained in the alkaloids extracted from Brazilian and Columbian ipecacuanha, these

drugs cannot be used in medicine as equally applicable, for whilst emetine has been found better than cephæline as an expectorant, the latter is superior as an emetic. The authors have, by methods already published, separated the bases in the ipecacuanha alkaloid from each kind, with the following results per 100 parts of each total alkaloid :—

| | Brazilian. | | Columbian. |
|---|---|---|---|
| | Root. | Stem. | |
| Emetine ............ | 72·14 | 65·6 | 40·5 |
| Cephæline ......... | 25·87 | 32·8 | 56·8 |
| Third Base ......... | 1·99 | 1·6 | 2·7 |

R. R.

**Physiological Action of Amidosulphonic Acid.** By N. Maeno (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, **2**, 487—493).—Plants of barley, *Brassica rapa, Allium fistulosum*, and soja bean were kept for some days in 0·1 and 0·05 per cent. amidosulphonic acid (as calcium salt). The plants all died after from 1 to 4 weeks. Branches of *Prunus domesticus* and leaves of *Æsculus turbinata* and of *Prunus cerasus* were also killed in a short time, similar branches and leaves remaining healthy in distilled water and in solutions of ammonium sulphate. The germinating power of seeds of rice, barley, soja bean, and turnips was also destroyed by dilute solutions of calcium amidosulphonate, but in different degrees, owing, perhaps, to the calcium salt penetrating into some more readily than into others.

The growth and fermentative power of yeast is not destroyed by amidosulphonic acid, but as a source of nitrogen the sulphonic acid is less favourable than ammonium sulphate.

As regards mammalia, the subcutaneous injection of 0·5 c.c. of 1 per cent. sodium amidosulphonate, into a white mouse, had no effect; on injecting a further 1 c.c., respiratory activity was considerably increased, but after 2 days the mouse was again in a normal condition. A mouse fed with bread soaked in the solution died; the amount of sulphonate consumed may, however, have been large. Loew found that lower aquatic animals remained alive in a 1 per cent. solution of the calcium salt. The sulphonic acid is less injurious to animals than the related carbamic acid (comp. Leo Errera, *Sur le mecanisme du sommeil*, Brussels, 1895).

Amidosulphonic acid is therefore exceptional as a poison, being poisonous neither to higher nor to lower animals, nor to fungi and algæ, whilst it destroys all kinds of phænogams. N. H. J. M.

**Action of Zinc on Red Wines.** By L. A. Levat (*Compt. rend.*, 1897, **124**, 242—243).—Zinc acts on red wines, destroying their bouquet and making them poisonous, without affecting the proportion of alcohol present. This metal should therefore not be used for the construction of receptacles, pipes, taps, &c., with which red wines are to come into contact. C. H. B.

**Cause of Increased Growth of Trees when Thinned.** By R. HORNBERGER (*Bied. Centr.*, 1896, **25**, 821—825; from *Forstl.-Naturwiss. Zeit.*, 1895, *Heft.* 11, 1—16).—If the increased growth of trees when thinned is due to the effect of light on the soil, resulting in the more rapid decomposition of the humus, rather than to the direct action of the light on the crowns of the trees, the wood of trees which have been thinned should be richer in ash constituents and nitrogen than that of trees which have not been thinned. It has frequently been shown that the outer wood is richer in minerals than the inner wood. The author now compares the composition of (1) the outer, (2) the intermediate, and (3) the inner wood of two beech trees over 100 years old, one of which (A) had, for 13 years, the advantage of increased light, the other (B) not. The numbers show the average results per thousand in the dry wood:

| | | | $K_2O$. | CaO. | MgO. | $Mn_2O_3$. | $P_2O_5$. | $SO_3$. | Total. |
|---|---|---|---|---|---|---|---|---|---|
| A | Inner | wood | 2·25 | 1·23 | 0·33 | 0·24 | 0·38 | 0·15 | 4·58 |
| | Intermediate | ,, | 1·94 | 1·50 | 0·47 | 0·33 | 0·24 | 0·21 | 4·69 |
| | Outer | ,, | 1·51 | 1·59 | 0·48 | 0·33 | 0·28 | 0·20 | 4·39 |
| B | Inner | ,, | 1·09 | 1·28 | 0·46 | 0·24 | 0·23 | 0·15 | 3·45 |
| | Intermediate | ,, | 2·33 | 1·08 | 0·35 | 0·17 | 0·42 | — | 4·35 |
| | Outer | ,, | 1·35 | 0·84 | 0·21 | 0·15 | 0·27 | 0·23 | 3·05 |

The results are opposed to those of Ebermayer, Weber, Schröder, Daube, and others, according to which the minerals decrease from the outside towards the centre. In both trees, the total ash is less in the outer than in the inner wood, and is greatest in the intermediate wood.

Comparing the outer wood of the two trees, there is a greater amount of each constituent, except phosphoric and sulphuric acids, in (A) than in (B). When the amounts of ash constituents of the outer wood are divided by the corresponding arithmetical means of those of the intermediate and inner wood, the quotients for (A), except in the case of potash, are greater than in (B). The difference is still more distinct if the outer and intermediate wood alone are considered. Under the influence of increased light, there was thus a greater percentage of mineral matter in the wood, notwithstanding that the production of wood was increased. There was also an increase in the amount of nitrogenous matter.

The results indicate that the increased production probably depended on an increased amount of available nutritive matter in the soil and increased activity of root fungi. N. H. J. M.

---

## Analytical Chemistry.

---

**Gas Analysis Apparatus.** By OTTO BLEIER (*Ber.*, 1897, **30**, 697—701).—A form of apparatus is described in which all the pipettes are permanently fixed to the measuring cylinder, communication being brought about by means of a many-way glass tap fixed at the head of the cylinder.

A new form of explosion pipette is also introduced, the essential feature being that the gas to be exploded is passed in a slow stream through a capillary tube, an expansion in the middle of which contains platinum wires for the passage of sparks or a platinum spiral which can be heated by an electric current. A modified form of this which admits of the introduction of potash solution is of service in the estimation of nitrogen in presence of argon, the gases mixed with oxygen being passed through the apparatus. J. F. T.

**New Glass for Collecting Sediments.** By EDUARD SPAETH (*Zeit. angw. Chem.*, 1897, 10—11).—This consists of an ordinary conical glass, provided at its lower end with a stopcock of peculiar construction. The glass is filled, say, with turbid water, and the deposit gradually collects in a hollow U-shaped space in the plug of the stopcock. By turning the latter in the proper direction, the water in the glass is cut off and may be thrown away. The stopcock can then be removed and the sediment subjected to microscopical examination. L. DE K.

**Estimation of Fluorine in Wines or Waters.** By QUIRINO SESTINI (*L'Orosi*, 1896, **19**, 253—258).—Carnot's method of determining fluorine (Abstr., 1892, 911), although somewhat long, gives results only about 1 per cent. less than that of Fresenius, but the method of Nivière and Hubert (*Mon. Scient.*, 1895, 324) gives very low results. The author has therefore devised the following rapid method of determining fluorine in wine: 100—200 c.c. of the wine is rendered slightly alkaline with sodium carbonate, and whilst boiling 2—4 c.c. of concentrated calcium chloride solution is added; the precipitate containing the calcium fluoride is ignited, mixed with precipitated silica, and placed in a U-tube about 12 inches high, which is fitted with side tubes. One arm, A, of the tube is provided with a dropping funnel, whilst the other arm has a large bulb blown on it near the top and is fitted with a thermometer; this arm is connected by the side tube with a smaller U-tube constricted at the bend, in which is placed recently filtered mercury, and, in the arm furthest from A, concentrated potassium fluoride solution. Whilst a current of dry air free from carbonic anhydride is passing through the apparatus from A, 20—30 c.c. of pure concentrated sulphuric acid is run in and the temperature gradually raised to 160°.

The air current carries the silicic fluoride into the second U-tube, and it is precipitated there as potassium silicofluoride by the fluoride solution; the latter, after half an hour's working, is poured out and diluted with an equal volume of 96 per cent. alcohol. The precipitate is collected after a few hours, washed with 60 per cent. alcohol, dried on a tared filter at 110°, and weighed. The method gives excellent results, and may also be used in the analysis of mineral waters.

W. J. P.

**Toxicological Examination for Free Ammonia.** By DISCORIDE VITALI (*L'Orosi*, 1896, **19**, 403—404).—In the toxicological examination for free ammonia, the author distils the solid and liquid material from a retort below 100°. The distillate, which contains the free ammonia, together with the carbonate and sulphide, is treated with

calcium chloride, and small quantities of lead carbonate are slowly added until the liquid ceases to become brown. After filtration, the liquid is again distilled, when the distillate contains only the free ammonia. W. J. P.

**Volumetric Estimation of Phosphoric and Arsenic Acids.** By A. C. CHRISTENSEN (*Zeit. anal. Chem.*, 1897, **36**, 81—96).—The author has succeeded in applying the iodimetric method to the estimation of both free and combined phosphoric acid, and has thus developed a volumetric method which vies with the gravimetric in accuracy. Free phosphoric acid, added to a mixture of potassium iodate and iodide, liberates iodine but slowly, and to a somewhat indefinite amount. When, however, bromate is substituted for iodate, the following reaction occurs with certainty: $KBrO_3 + 6KI, + 6H_3PO_4 = 6KH_2PO_4 + 3I_2 + KBr + 3H_2O$. At ordinary temperatures, the action requires 24 hours, but at 40—50° it is complete in half an hour. For accurate results, the following conditions must be observed. The thiosulphate should be standardised against N/10 sulphuric acid, under conditions resembling those of a phosphoric acid estimation. Not more phosphoric acid should be taken than will correspond with 40 c.c. of N/10 thiosulphate. Not less than 0·5 gram of bromate and 3 grams of potassium iodide must be used, and the volume must be kept between 100 and 120 c.c. To estimate combined phosphoric acid, it is necessary to convert it into a normal alkali phosphate. When analysing calcium phosphates, this may be done by precipitating the phosphoric acid as silver phosphate, which is then decomposed by a small excess of sodium chloride. The phosphate (previously ignited, since organic matter is prejudicial) is dissolved in nitric acid and treated with an excess of silver nitrate, avoiding too great dilution. To the warm mixture, soda solution is then added until a permanent precipitate is formed, but avoiding precipitation of brown silver oxide. A 10 per cent. solution of ammonia is then dropped in until the precipitate ceases to augment and the liquid has become alkaline. The mixture is then boiled for 5—10 minutes. After allowing it to deposit, the precipitate is collected on a small filter, and washed with a 2—3 per cent. solution of potassium nitrate until free from calcium. The filter and contents are returned to the precipitation flask, and treated with sodium chloride. The solution is filtered into a stoppered bottle, and the silver chloride washed with the potassium nitrate solution until the washings are no longer alkaline. There is then added 50 c.c. of N/10 sulphuric acid and the treatment with bromate and iodide proceeded with as above. Since the reaction of sulphuric acid with the normal phosphate liberates a tribasic acid, which, however, with the bromate and iodide, reacts as a monobasic one, it follows that the difference between the c.c. of N/10 sulphuric acid taken and of N/10 thiosulphate required gives, when multiplied into 0·0049 (the half-milligram molecule of $H_3PO_4$), the amount of phosphoric acid present.

In presence of iron, the silver method is inapplicable. The phosphoric acid must in that case be precipitated as ammonium magnesium phosphate, and this, after washing first with ammonia and then with

90 per cent. alcohol to displace the free ammonia, is rinsed from the filter into the stoppered bottle and dissolved in the measured quantity of N/10 sulphuric acid. Equally good results were obtained, whether the precipitation by magnesia was preceded by the molybdate method or the citrate process was adopted for preparing the magnesium precipitate directly.

A precisely similar method is applicable to arsenic acid, but with results of somewhat inferior accuracy, especially when using the silver process. When, however, the arsenic acid is first converted into ammonium magnesium arsenate, and Puller's correction for the solubility of this salt in the ammoniacal wash water (1 milligram per 30 c.c.) is applied, the results agree well with theory. M. J. S.

**Estimation of Pyrophosphoric Acid.** By MARCELLIN P. E. BERTHELOT and GUSTAVE ANDRÉ (*Compt. rend.*, 1897, **124**, 261—265). —The precipitate formed by the action of magnesia mixture on solutions of pyrophosphoric acid in presence of acetic acid (this vol., ii, 158) has the composition $Mg_3(NH_4)_2(P_2O_7)_2 + nH_2O$, about one-quarter of the ammonium being, however, displaced by sodium. The ammonium in the precipitate has no recognisable tension of dissociation, and is not expelled when the precipitate is dried in a vacuum or when it is heated at 110°. If the precipitate is subjected to prolonged washing with dilute acetic acid, it is partially decomposed, magnesium being eliminated more rapidly than phosphoric acid. The presence of a large proportion of ammonium salts in the liquid in which the precipitate is formed is essential, otherwise the ratio of magnesium to phosphoric acid alters, and precipitation of the latter is less complete.

It is noteworthy that sodium metaphosphate, whether prepared at a high or low temperature, yields exactly the same precipitate as the pyrophosphate under the same conditions, a result due to the readiness with which the metaphosphate is converted into pyrophosphate.

C. H. B.

**Volumetric Estimation of Boric Acid.** By GUNNER JÖRGENSEN (*Zeit. angw. Chem.*, 1897, 5—7).—Hönig and Spitz having doubted the accuracy of the author's process (Abstr., 1896, ii, 449), he once more gives full details of the method. To estimate boric acid in milk, 100 c.c. of the sample is evaporated with a small quantity of sodium carbonate, the residue charred, and the carbon burned off as far as possible; the ash is digested for some time in dilute sulphuric acid to expel any carbonic anhydride, and the liquid, filtered from any undissolved charcoal and after adding phenolphthalein, is carefully neutralised with soda solution so as to precipitate the phosphates of the alkaline earths. To this liquid, which should not exceed 50 c.c., 20 c.c. of glycerol is added, and then standard soda, checked against boric acid, is run in until the solution becomes pink. The results are accurate, but if only very small quantities of boric acid are likely to be present, it should first be carefully tested for qualitatively. L. DE K.

**Estimation of Boric Acid by Gooch's Method, and Analyses of Colemanite and Pandermite [Priceite].** By KARL KRAUT (*Zeit. anal. Chem.*, 1897, **36**, 165—167).—In consequence of the want of agreement

amongst analysts as to the trustworthiness of this method (Abstr., 1887, 299), the author gives the details of his mode of performing it, together with the results obtained in the analyses of the above native borates.

About 2—2·5 grams of lime is ignited to constant weight in a platinum crucible. The greater part is shaken out into a flask of 200 c.c. capacity, and made into a milk with water. A second flask, of the pattern used for Kjeldahl nitrogen estimations, receives the weighed borate, and is then fitted with a stopcock funnel, whilst its delivery tube dips into the milk of lime. The lime flask is kept cold. A suitable quantity of nitric acid is first introduced and distilled over, by the heat of an oil bath, then 6—8 successive quantities of methylic alcohol of 10 c.c. each, interposing at intervals the addition and distillation of 1 c.c. of water. The contents of the receiver are evaporated in a platinum basin on the water bath at the lowest possible temperature, and returned to the original platinum crucible, using nitric acid for rinsing the vessels, and then, by exposure to a gradually increasing temperature, dried and ignited, finally in a Hempel's furnace, until the weight remains constant.

Colemanite, analysed by this process, the calcium being estimated after expelling the boric acid, and the water by ignition under a layer of lime, gave numbers closely agreeing with the formula $2CaO,3B_2O_3,5H_2O$; whilst pandermite [priceite] (the specimen of which was free from sulphuric acid, barium, strontium, and magnesium) gave $4CaO,5B_2O_3,7H_2O$.

M. J. S.

**Elementary Analysis in the Berthelot Calorimetric Bomb.** By K. Kroeker (*Ber.*, 1897, **30**, 605—607).—In order to obtain useful results as to the heating effect of fuels by means of the calorimetric bomb, it is necessary to determine the amount of water formed by the combustion. This may be readily done, and with sufficient accuracy, by providing the bomb with two passages through the top by means of which a current of air can be passed through the instrument at the close of a combustion, and the water which has been formed weighed in the usual manner. Experiments made with pure sugar show that this can be done even in the presence of such amounts of sulphuric acid as might be formed by the combustion of coal.

A. H.

**Simplification of Schweitzer and Lungwitz's Method of Estimating Potassium.** By Adolf Mayer (*Zeit. anal. Chem.*, 1897, **36**, 159—163).—The estimation of potassium in such substances as fertilisers, which contain sulphates, phosphates, iron, alkaline earths, &c., has hitherto required a somewhat complicated procedure for removing these impurities before the treatment with platinic chloride could be applied. Schweitzer and Lungwitz have sought to simplify this purification, by treating the solution of the original substance with a solution of barium oxalate in hydrochloric acid in sufficient quantity to precipitate all the sulphates, and then, after oxidation of the iron by hydrogen peroxide, adding an excess of ammonia, by which means the alkaline earths originally present, as well as the excess of barium added, are removed as oxalates, whilst the heavier metals are precipitated as hydroxides. A single filtration, therefore, gives a solution which only requires the expulsion of the ammoniacal salts.

Schweitzer and Lungwitz recognised that the hydrochloric acid solution of barium oxalate might be replaced by a mixture of barium chloride and oxalic acid, but they deprecated this substitution on the ground that the exact equivalence of the barium and oxalic acid ought to be ensured. The author points out that this exactitude is needless, provided care is taken that enough oxalic acid is present to precipitate all the bases. In place, therefore, of Schweitzer and Lungwitz's solution, he adds first a sufficient volume of normal barium chloride solution, and then an equal volume of normal oxalic acid, and thus overcomes one of the objections to the original process, namely, that the sparing solubility of barium oxalate in hydrochloric acid entailed the use of large volumes of reagent and a corresponding amount of evaporation. An objection to all forms of this process is, however, that, after adding the barium oxalate, the mixture must be boiled for fully 20 minutes. The time and attention which this requires constitute a substantial set-off against the simplification in other directions. M. J. S.

**Estimation of Caustic Alkalis in the Presence of Alkali Carbonates.** By Georg Lunge (*Zeit. angw. Chem.*, 1897, 41—42).—The author recommends titrating with standard hydrochloric acid, using methyl-orange as indicator, which gives the total alkali present, the carbonic anhydride being estimated in another portion of the liquid by means of the apparatus devised by Lunge and Marchlewski. When dealing, however, with a mixture containing comparatively little carbonate, the titration may be effected with sufficient accuracy by the well known method of titrating with methyl-orange and also with phenolphthalein; in presence of larger quantities of carbonates, however, the barium chloride method as devised by Winkler is preferable.

L. de K.

**Delicate Test for Copper.** By A. Jaworowsky (*L'Orosi*, 1896, 19, 195—196).—On adding excess of ammonia and 1 or 2 drops of phenol to a liquid (5 c.c.) containing traces of copper and agitating, it slowly becomes turbid and blue; the coloration becomes more intense on standing for upwards of an hour. On shaking with ether, the liquid clears but preserves its colour, and the precipitate collects at the boundary between the two liquids; no other metal of the fifth group gives this reaction. W. J. P.

**Detection of Copper in Vegetable Substances.** By Benjamin H. Paul and Alfred J. Cownley (*Pharm. J. Trans.*, [iv], 2, 441—442).—About 100 grams of the material is carbonised in platinum, the ash extracted with strong hydrochloric acid filtered, and the filtrate and washings of the ash collected in a porcelain dish. The insoluble residue is then treated with a few drops of strong nitric acid, dried, and ignited, the ignited mass being digested with strong hydrochloric acid, filtered, and the filtrate added to the former portion. The whole is evaporated down to about 30 c.c. and placed in a weighed platinum dish in which the copper is precipitated by pure zinc, dried, and weighed. If the copper appears to be impure, it may be dissolved in a little nitric acid and estimated colorimetrically. In 10,000 parts of the following alimentary substances, the authors'

results gave the minimum and maximum quantities of copper named:—Oysters (4 samples), 1·81—3·03; cocoa (3 samples), 0·29—0·58; spirits (5 samples), 0·01—0·05; preserved peas (11 samples), 0·54—1·44.

R. R.

**Estimation of Iron in Urine.** By ADOLF JOLLES (*Zeit. anal. Chem.*, 1897, 36, 149—158).—The few investigators who have occupied themselves with this enquiry have arrived at very discordant results, in consequence, doubtless, of the errors incidental to the estimation of the very small amount normally present. Incineration being unavoidable, the following method is recommended. Five hundred c.c. of the urine, after being concentrated first on the water bath, and then in an air bath at 180° until the residue has sintered, is moistened with absolute alcohol and the alcohol set on fire. The basin is then gradually heated over a bunsen flame as long as volatile matter is given off, and the dark grey residue is rubbed to fine powder with a pestle, and transferred to a Berlin porcelain crucible, the last portions being removed by means of nitric acid; the residue is then dried and burnt to a white ash in a muffle. Platinum vessels must not be used. The ash is now completely exhausted with hot water and the insoluble residue fused with potassium anhydrosulphate. The solution is preferably reduced by zinc and titrated with permanganate, but since even the purest zinc obtainable contains traces of iron, known amounts (2 grams) must be used and the iron thus introduced allowed for. For gravimetric estimation, Gottlieb has recommended a process based on precipitation of the iron by potassium ferrocyanide, but the method, although exact, is tedious, and requires considerable analytical skill. A much more convenient precipitant is nitroso-$\beta$-naphthol, by a solution of which in 50 per cent. acetic acid the iron in a hydrochloric acid solution of urine ash is completely precipitated as pure ferric nitrosonaphthol $Fe(C_{10}H_6NO_2)_3$ (compare this vol., ii, 163). The reagent is prepared by dissolving 1·2 gram of pure crystallised nitroso-$\beta$-naphthol in 100 c.c. of 50 per cent. acetic acid at about 90°. The insoluble matter of the urine ash is heated with concentrated hydrochloric acid, which dissolves the iron completely; a small excess of the reagent is then added, the mixture stirred for 5 minutes, and, after 5 minutes' subsidence, it is filtered and the precipitate washed with 50 per cent. acetic acid until the washings are feebly yellow. The further treatment of the precipitate is not described. The urine of 12 healthy persons, examined by one or other of the above methods, side by side with Gottlieb's and Hamburger's methods (the latter a titration by permanganate after reduction by sulphurous acid) showed a total excretion ranging from 4·6 to 9·6 (average 8·0) milligrams of iron in 24 hours. Gottlieb (*Arch. für experiment. Pathol. u. Pharmakol.*, 26, 139) found an average of 2·59 milligrams.

M. J. S.

**Separation of Glycerol from Wines by Means of Steam.** By FRÉD. BORDAS and SIG. DE RACZKOWSKI (*Compt. rend.*, 1897, 124, 240—242).—Fifty c.c. or 25 c.c. of the wine is placed in a flask of 300 c.c. capacity which is immersed up to the neck in a saturated solution of sodium chloride. The alcohol is completely distilled off at 110° under reduced pressure, and a slow current of steam is passed through

the liquid (still under reduced pressure) for 3 hours. The distillate is collected in two Woulff's bottles, and the rise of temperature in the receivers is sufficient to expel all the alcohol and a large part of the water, but direct experiments show that no glycerol escapes from the second bottle. The contents of the two bottles are mixed, diluted to 250 c.c. or 500 c.c., and the glycerol estimated by means of potassium dichromate as previously described (this vol., ii, 193). The results are concordant, and agree fairly well with those obtained by Pasteur's method, but are always higher. C. H. B.

**Detection and Estimation of Cane-sugar in Wine.** By PAUL KULISCH (*Zeit. angw. Chem.*, 1897, 45—47, 205—210).—A criticism of the conventional method adopted in Germany. The author points out that the amount of hydrochloric acid used for the inversion of the sugar is too small, as part of it is neutralised by the alkali added before the wine is submitted to distillation.

It is now proposed to use oxalic acid; 1 gram to 50 c.c. of the sample previously diluted with an equal bulk of water, or 2 grams to 50 c.c. of undiluted wine. The inversion is complete after 30 minutes' heating on the water bath. L. DE K.

**Examination of Wine for Impure Starch-sugar.** By LEO GRÜNHUT (*Zeit. anal. Chem.*, 1897, **36**, 168—176).—The conventional methods (*Zeit. anal. Chem.*, **35**) for the examination of wines containing more than 0·1 gram of total sugar in 100 c.c., involve the complete fermentation of the wine and the precipitation of the residue with alcohol (compare Abstr., 1882, 999), a procedure which, in many cases (for example, in all young wines), would prolong the analysis to an inadmissible extent. It is, however, quite easy, by a comparison of the specific rotatory power of a wine with its copper-reducing power, to select those cases where a fermentation is unavoidable. The residual unfermented sugar in natural wines being a mixture of invert-sugar and levulose, the value of $[\alpha]_D$ must lie between $-20·2°$ and $-93·3°$, and experience shows that it is uually between $-45°$ and $-90°$, and approaches the latter number the more nearly as the percentage of sugar falls. The presence of cane-sugar, maltose, isomaltose, or dextrin would reduce this lævorotation, or even convert it into a dextrorotation. If, now, the amount of a sugar is estimated by its copper-reducing power and calculated as invert-sugar, it follows, from the fact that all the above sugars, &c., reduce less copper than invert sugar, that their apparent specific rotatory power would calculate out higher than their true rotatory power. That of cane-sugar, which reduces no copper, would be $+\infty$; that of dextrin about $+3190°$. The following change in the "instructions" is therefore suggested, "If more than 0·1 gram of reducing sugar per 100 c.c. has been found, its apparent specific rotation is calculated by the formula $[\alpha]_D = \frac{100\,a}{2(c - 0·1)}$ where $a$ is the angle of rotation for sodium light by a 200 mm. column, and $c$ the number of grams of reducing sugar in 100 c.c. Should the value for $[\alpha]_D$ thus found be positive or lie between 0 and $-45°$, the wine may contain cane-sugar, or impure starch-sugar or both. In that case, a further examination for starch sugar is to be

made." The subtraction of 0·1 from the value of $c$ is made because thoroughly fermented wine still contains that amount of reducing substances, which, however, are not optically active.

As a further improvement on the official process, the author suggests the use of a minimal quantity of pure-culture wine yeast instead of the 5 grams of beer yeast specified, in order to avoid a dark colour in the concentrated syrup. M. J. S.

**Sweet Wines.** By WILHELM FRESENIUS (*Zeit. anal. Chem.*, 1897, **36**, 102—148).—In this important communication, the author publishes the results of the analyses of about 150 specimens of sherry, madeira, marsala, port, Cape, Malaga, Greek, Hungarian, and artificial wines, of which, in most cases, the origin was authenticated. The paper does not admit of serviceable abstraction. One of the most remarkable specimens examined was a Malaga wine (No. 19), which, although of almost unquestionable genuineness, exhibited a dextrorotatory polarisation of $+1·8°$, and presented all the analytical characteristics of a wine adulterated with starch sugar. On further examination, it yielded an unfermentable dextrorotatory constituent, which reduced more Fehling's solution after inversion than before. This is supposed to owe its origin to the boiling of the must (compare Bornträger, *Zeit. angw. Chem.*, 1892, 207). M. J. S.

**Estimation of Formaldehyde.** By RONALD ORCHARD (*Analyst*, 1897, **22**, 4).—The liquid containing the formaldehyde, which must be free from other reducing substances, is boiled with an ammoniacal solution of silver nitrate for 4 hours in a conical flask furnished with a reflux condenser. The precipitated metallic silver is then collected and weighed. Its weight multipled by 0·0694 represents the formaldehyde. L. DE K.

**Separation and Estimation of Formaldehyde.** By NORMAN LEONARD and HARRY M. SMITH (*Analyst*, 1897, **22**, 5—6). Formaldehyde, although very volatile, cannot be completely separated from its aqueous solution by distillation unless this is continued almost to dryness; for this reason, it is very difficult to recover anything like the amount added to milk.

When dealing with milk, it is best to slightly acidify with sulphuric acid before submitting it to distillation. In one experiment cited by the authors, 0·0090 gram of formaldehyde was added to 100 c.c. of milk, and 0·0056 gram was recovered from the first 60 c.c. of the distillate; the residue showed, however, a trace by Hehner's test. The estimation of the aldehyde, previously described by Smith, is based on its reducing action on potassium permanganate in alkaline solution.

When the milk is sour and decomposed, it may yield a distillate containing organic compounds, and consequently would reduce permanganate; in such cases, the process is untrustworthy. L. DE K.

**Toxicological Detection of Hydrocyanic Acid.** By F. FILSINGER (*Chem. Zeit.*, 1896, **20**, 305).—The author calls attention to the great delicacy of the guaiacum copper sulphate test for hydrocyanic acid.

Even when the Prussian blue and the thiocyanate test are unsatisfactory, a fine blue colour may still be obtained with the above reagent.

L. DE K.

**Estimation of Stearic Acid in Fats.** By OTTO HEHNER and CHARLES A. MITCHELL (*Analyst*, 1896, **21**, 316—331).—A lengthy investigation of various points concerned in this estimation containing a large amount of most valuable detail, accompanied by tables. The following process is finally recommended :—Alcohol of sp. gr. 0·8183 at 0° is saturated with pure stearic acid at 0°. From 0·5 to 1 gram of solid, or about 5 grams of liquid, fatty acids is dissolved in about 100 c.c. of the alcohol, and allowed to remain in an ice-bath overnight. The separated stearic acid is collected, washed with the cold spirit, dried, and weighed. Its melting point should not be much less than 68·5°.

L. DE K.

**Estimation of Free Fatty Acids in Fats and Oils.** By WM. WALTKE (*Chem. Zeit.*, 1896, **20**, 480).—The usual practice is to heat 10 grams of the sample, freed from mineral acids by treatment with hot water, with about 30 c.c. of alcohol, and to titrate with standard soda, using phenolphthalein as indicator ; 1 c.c. of normal soda equals 0·28 gram of free fatty acid. For most fats, this factor is accurate enough ; but when testing coco-nut oil, it cannot be used, as the factor depends on the molecular weights of the fatty acids, which, for this oil, vary from 205 to 240. The molecular weight of any given sample is, however, readily obtained by isolating the fatty acids and titrating a known weight of the dried acids with $n/5$ soda in alcoholic solution.

L. DE K.

**Estimation of Potassium Hydrogen Tartrate in Wines.** By HENRI GAUTIER (*Compt. rend.*, 1897, **124**, 298—300).—One hundred c.c. of the wine is concentrated to about 15 c.c. and allowed to remain for two or three days in a cool place at a fairly constant temperature, a flask containing a saturated aqueous solution of potassium hydrogen tartrate being placed near it. The wine residue is filtered through a small filter into a graduated measure, in order that the volume of the liquid may be ascertained. The precipitate on the filter is washed with the saturated solution of potassium hydrogen tartrate, and is then transferred to a flask, mixed with a volume of the hydrogen tartrate solution exactly equal to the volume of the filtrate from the wine residue, diluted to about 100 c.c. with water, heated gently to dissolve the salt, and titrated with potassium hydroxide solution, using phenolphthalein as indicator.

A correction is necessary, because the solubility of potassium hydrogen tartrate in water is greater than its solubility in the wine residue, and this correction is independent of the source of the wine. It amounts to 0·15 gram of potassium hydrogen tartrate per litre for every 10 c.c. of concentrated wine residue, and this must be subtracted from the quantity found by the author's method. C. H. B.

**Colour Reactions of Organic Acids, principally Tartaric, Citric, and Malic.** By EUGENIO PIÑERÚA (*Chem. News*, 1897, **75**, 61; and *Compt. rend.*, 1897, **124**, 291—292).—0·5 gram of the organic acid is

carefully heated with 10 to 15 drops of a fresh solution containing 0·02 gram of β-naphthol in 1 c.c. of sulphuric acid, sp.gr. 1·83. Tartaric acid gives at first a blue coloration changing to green, and on mixing, when cool, with 15 to 20 vols. of water, it becomes reddish-yellow. Citric acid gives a blue that does not change to green unless tartaric acid is also present; on diluting, it becomes colourless or faintly yellow. Malic acid gives at first a greenish-yellow, becoming bright yellow, and on diluting bright orange. Other organic acids give less distinct and characteristic reactions; nitrites, nitrates, and chlorates also produce colour reactions; thus sodium nitrite gives a very strong red, unchanged by dilution. A solution containing 0·1 gram of resorcinol in 1 c.c. of sulphuric acid (66°) gives a reddish-brown, becoming an intense violet on further heating, and orange on dilution; with sodium or potassium nitrate and with potassium chlorate an intense green, changing to brown on dilution. D. A. L.

**Identification of Citric Acid.** By LUDV. STAHRE (*Zeit. anal. Chem.*, 1897, **36**, 195; from *Nordisk Famaceutisk Tidskrift*, **2**, 141).—The test is based on the fact that citric acid, on oxidation, yields acetone, which, by the action of bromine, is converted into bromacetone. The solution to be tested is mixed with a few drops of permanganate and warmed (but not to boiling) until the red colour has disappeared. A few drops of bromine water are then added, when a white turbidity or precipitate is produced, either immediately or on cooling. As little as 0·2 milligram of citric acid in 1 c.c. still yields an opalescence. On adding soda, the well known odour of bromoform is evolved. The bromine may also be added before the permanganate, and in that case less permanganate is required. This form of the test should be used when tartaric or malic acid is present. Malic acid produces the odour of bromoform on addition of soda; tartaric acid does not.

M. J. S.

**Testing Lemon Oil.** By HENRY GARNETT (*Pharm. J. Trans.*, 1896, [iv], **2**, 323).—The quantitative determination of the citral in lemon oil is stated to be the most trustworthy test of its value, and the author now proposes a process for this estimation founded on the reduction of citral to geraniol, and the conversion of the latter into its acetate, which admits of saponification by a standard solution of potassium hydroxide. The reduction of the citral is effected by dissolving the lemon oil in an equal volume of glacial acetic acid, and gradually and cautiously adding metallic sodium (5 grams for 20 c.c. of oil). The cooled liquid is diluted, transferred to a separator, the oil washed free from acid, dried, boiled with acetic anhydride to convert it into its acetate, washed until neutral, dried by contact with anhydrous sodium sulphate, and the whole, or a portion, taken for hydrolysis with excess of normal alcoholic potash, the excess of alkali being then titrated. 6·49 to 7·07 per cent. of citral was found in samples of pure lemon oil. R. R.

**Testing the Purity of Rose Oil.** By ROBERT JEDERMANN (*Zeit. anal. Chem.*, 1897, **36**, 96—102).—The tests hitherto depended on for detecting the presence of geranium oil, namely, the sulphuric acid test and the solidifying temperature, are shown to have a very limited value.

Two forms of the sulphuric acid test are in current use. The German Pharmacopœia prescribes mixing 5 drops of the oil with 25 drops of pure concentrated sulphuric acid, and the subsequent addition of 10 c.c. of alcohol of 0·81 sp. gr. The American Pharmacopœia uses only 5 drops of sulphuric acid and 2 c.c. of alcohol. Geranium oil under these conditions gives a markedly turbid solution, whilst genuine rose oil is supposed to give a colourless and nearly clear one. An extensive experience of genuine East Roumelian rose oil shows that comparatively few specimens will pass this test. The turbidity is due to the presence of traces of resinous substances which distil over with the oil, and under some circumstances may increase markedly in amount, without, however, impairing the fineness of the article as a perfume. Equally little is a high solidifying point to be trusted as evidence of high quality. It may, indeed, indicate the absence of geranium oil, but is also compatible with the presence of an unduly large proportion of the inodorous stearoptene. In consequence of conditions obtaining during the distillation, the limits 17·5—20° usually adopted may be widely deviated from in both directions. The index of refraction is a more trustworthy indication. The average for genuine oil at 30° may be taken as 43° 30′, whilst that of geranium oil is 41° 30′. Further, at 30°, the specific gravity of rose oil varies only between 0·8555 and 0·8645, whilst that of geranium oil is 0·883—0·8895. Although a combination of the above tests may furnish presumptive evidence as to genuineness, yet a careful attention to the odour, and to the practical results obtained in the application to perfumery, are the most satisfactory guarantees of quality. M. J. S.

**Essential Oils of Black and White Peppermint.** By John C. Umney (*Pharm. J. Trans.*, 1896, [iv], **2**, 123—125).—The oil of white peppermint may be distinguished from that of black peppermint by its greater optical activity; its not depositing menthol at a low temperature; its containing a greater proportion of menthol acetate and isovalerate, and by its giving an intense blue coloration with coppery fluorescence when it is mixed with 3 parts of glacial acetic acid and allowed to remain some hours; the black peppermint oil gives only a very pale colour. R. R.

**Detection of 'Rosin Oil' in Fatty Oils.** By Cornette (*L'Orosi*, 1896, **19**, 234—235).—"Rosin oil" is sometimes used as an adulterant of fatty oils; its presence may be detected by saponifying 10 c.c. of the oil with soda, dissolving the soap in hot water, and adding excess of concentrated sodium chloride solution after cooling. The sodium salt of the fatty acid is thus precipitated, whilst the sodium salt derived from the rosin oil remains dissolved; the liquid is filtered, the precipitate washed with salt solution, and the rosin oil acids liberated from the clear filtrate by sulphuric acid. The acids soon solidify, and may be collected on a tared filter and weighed. W. J. P.

**Rancidity of Olive Oil.** By Quirino Sestini (*L'Orosi*, 1896, **19**, 361—367).—From determinations of the total and free acidity of 35 samples of olive oil, the author concludes that the acidity number is no criterion of the state of rancidity of olive oil. W. J. P.

**Discrimination between Boiled and Unboiled Linseed Oil.** By Giulio Morpurgo (*L'Orosi*, 1896, **19**, 373—374).—Of late years, drying oil has been prepared in England by treating with oxygen in a special apparatus linseed oil in which rosin has been dissolved; the prepared oil is only distinguished with difficulty from the unboiled oil, as it contains no metallic oxides in solution, as in the case of ordinary drying oil. The author saponifies 20 c.c. of the oil with a slight excess of soda, then adds excess of sodium chloride to the aqueous solution, and after a time filters off the soap; the filtrate from boiled oil becomes turbid on adding acetic acid, whilst that from the unprepared oil remains nearly or quite clear. W. J. P.

**The Iodine Number of Oils.** By Hugo Mastbaum (*Zeit. angw. Chem.*, 1896, 719—721).—The iodine number of an oil is always higher when the sample is a cold-pressed one. In their investigations of the iodine number of linseed oil, van Ketel and Amtusch made use of oil extracted by means of light petroleum, and consequently got an article containing more stearin than the commercial oil, and giving therefore a somewhat lower Hübl figure. L. de K.

**Estimation of Antipyrine.** By Carl Kippenberger (*Zeit. anal. Chem.*, 1896, **35**, 659—677).—Phenyldimethylpyrazolone, known in commerce as antipyrine, analgesine, anodynine, metozine, parodyn, phenylone, sedatine, or phenazone, is completely precipitated either from neutral or (mineral) acid solutions by iodine dissolved in potassium iodide, the product being a periodide of the composition $C_{11}H_{12}N_2O,HI,I_2$. Manseau's method of titration is based on this fact, but the conditions under which he worked did not afford correct results. Neutral solutions, or solutions acidified with hydrochloric acid, consume considerably more than the theoretical amount of iodine, but when the antipyrine is first converted into hydriodide by the addition of hydriodic acid, or when sufficient hydriodic acid is present in the iodine solution, exactly 2 atoms of iodine are consumed by 1 molecule of antipyrine. A measured quantity of the approximately 1 per cent. antipyrine solution is therefore mixed in a dry stoppered bottle with a small excess of N/20 iodine solution made with 10 grams of potassium iodide and 40 c.c. of 52 per cent. hydriodic acid (sp. gr. 1·7) in the litre. After shaking until the periodide has collected as a tarry mass of dark brown colour, and the supernatant liquid has become clear, the mixture is filtered through purified asbetos into a dry burette, and in an aliquot part the excess of iodine is titrated by N/20 thiosulphate. The results are sufficiently exact for most purposes, but in consequence of a slight solubility of the precipitate in hydriodic acid and iodide solutions, absolutely exact results can only be obtained by standardising the iodine solution against known amounts of antipyrine. Special experiments were made to ascertain whether acetanilide, phenacetin, sulphonal, aniline, or cane-sugar would disturb the results, but all were found to be without influence, especially if the solution is feebly acidified with hydrochloric acid. M. J. S.

**Micro-crystallographic Detection of Alkaloids.** By Vadam (*J. Pharm.*, 1896, [6], **4**, 485—488).—The author makes use of the following reagents. 1. Mayer's reagent. 2. Bouchardat's reagent (dilute solution of iodine in potassium iodide). 3. Saturated solution

of picric acid. 4. Gold chloride (1 : 20). 5. Platinic chloride (1 : 20). 6. Schulze's reagent (sodium phosphantimonate). 7. Sodium phosphotungstate. 8. Cadmium iodide (1 : 10). 9. Saturated solution of potassium dichromate. 10. Do. of potassium ferrocyanide. 11. Do. of potassium ferricyanide. 12. Sodium nitroprusside (1 : 10).

The alkaloid residue obtained by any of the usual methods of extraction, is weighed and dissolved in hydrochloric acid (diluted to 1/50) in such a manner as to give an alcoholic solution of about 1/200.

A dozen object glasses are placed in a row. A drop of the alkaloidal solution is put on each, and then a drop of the various reagents is added. Cover slips are put on, and the 12 slides, after being allowed to stand for half-an-hour, are examined microscopically with a low power, and the results noted. J. J. S.

**Kruger and Wulff's Method of Estimating Xanthine-bases in Urine.** By KARL H. HUPPERT (*Zeit. physiol. Chem.*, 1897, **22**, 556—560).—Precipitation of xanthine bases in the urine by cuprous salts as recommended by Krüger and Wulff gives results which are too high, because other constituents of the urine are carried down as well. Haycraft's silver method is recommended. W. D. H.

**Estimation of Caffeine in Tea, Coffee, &c.** By A. DELACOUR (*J. Pharm.*, 1896, [6], **4**, 490—491).—The author recommends the following method. Two grams of the finely divided substance is boiled with 80—90 c.c. of distilled water for some 10 minutes in a 100 c.c. flask; when cold 4 c.c. of lead acetate solution is added, the solution made up to the mark, shaken, and then filtered. Fifty c.c. of the clear filtrate is placed in a separating funnel, 10—15 drops of acetic acid added, and the mixture extracted four times with 20—25 c.c. of chloroform, the chloroform extracts are run into a tared flask, the chloroform slowly evaporated, and the residue dried and weighed. J. J. S.

**Estimation of Morphine in Opium.** By GUSTAV LOOFF (*J. Pharm.*, 1896, [6], **4**, 312).—The author finds that sodium salicylate readily precipitates the resinous matter contained in opium extract, and also a part of the narcotine. The morphine can then be precipitated from the clear filtrate by means of ammonia and a little ether. After stirring for some 10 minutes, a white precipitate is obtained; the small quantity of narcotine contained in this can be removed by means of benzene after the precipitate has been dried. J. J. S.

**Modification of De Vrij's Chromate Process.** By LEONARD DE KONINGH (*Ned. Tydschr. Pharm.*, 1897, 97—98).—The original method does not provide for the presence of cupreine sulphate in commercial quinine sulphate. The following modification is proposed. Two grams of the sample is dissolved in 80 c.c. of hot water, and mixed with 12 c.c. of a 5 per cent. solution of pure potassium chromate. When cold, the liquid is filtered, and 5 c.c. of a 10 per cent. solution of soda is added to the filtrate, when an immediate precipitate or turbidity will prove the presence of cinchonidine, quinidine, cinchonine, or hydroquinine. After filtering, the liquid is freed from traces of these alkaloids by agitating twice with ether or, better, chloroform (first 10 and then 5 c.c.)

and after adding 2 grams of ammonium chloride, it is again agitated repeatedly with chloroform, which dissolves the cupreine; this is left on evaporating the solvent, and may then be further tested. L. DE K.

**Detection of Aconitine.** By WYNDHAM R. DUNSTAN and FRANCIS H. CARR (*Pharm. J. Trans.*, 1896, [iv], 2, 122—123).—When a solution of an aconitine salt is mixed with a very slight excess of a solution of potassium permanganate, a purple, crystalline precipitate is produced which is fairly stable, especially in presence of a small quantity of acetic acid. In very dilute solutions, the precipitate appears after standing and stirring, as in the case of a 0·025 per cent. solution; but a 0·05 per cent. solution gives an immediate precipitate. It is possible to detect 0·000025 gram of aconitine by this means. Other alkaloids which give precipitates with the permanganate behave differently in this reaction. Cocaine salts are not distinctly precipitated in solutions containing much less than 1 per cent. of the alkaloid, and although the precipitate is crystalline, it is readily dissolved by water, as is that of hydrastine, which is not crystalline, and is pinker than the aconitine compound. The same is true of papaverine. Pseudaconitine most nearly resembles aconitine in this respect, but it is not precipitated readily in solutions containing much less than 0·5 per cent.; the precipitate dissolves when the liquid is heated, and separates out on cooling, whereas the aconitine precipitate rapidly darkens when warmed. Aconine salts are not precipitated by the permanganate, nor is a 1 per cent. solution of benzaconine acetate. R. R.

**Estimation of Aconitine.** By WYNDHAM R. DUNSTAN and THOMAS TICKLE (*Pharm. J. Trans.*, [iv], 2, 121).—Pure aconitine may be very accurately estimated by heating its sulphate in a closed tube with water at 125° for 3 hours, when it undergoes partial hydrolysis with production of one molecular proportion of acetic acid and the separation of a little benzoic acid. The liquid, as taken from the tube, is made alkaline with pure sodium hydroxide, and the alkaloid is removed by twice shaking with chloroform; the aqueous liquid is acidified with sulphuric acid, and the benzoic acid removed by agitation with benzene, after which it is distilled until the whole of the acetic acid has come over, when the distillate is titrated with baryta water, using phenolphthalein as the indicator. This method is, however, quite inapplicable to the total alkaloid obtained from the root of *Aconitum napellus* and the preparations from it, because certain amorphous, inseparable alkaloids which are present also yield acetic acid. From a mixture of these amorphous bases, which would probably contain less than 5 per cent. of aconitine, the acetic acid produced corresponded with 34 per cent. It follows that the galenical preparations made from *A. napellus* cannot at present be standardised. R. R.

**Estimation of Total Alkaloids in Coca Leaves.** By ALEXANDER GUNN (*Pharm. J. Trans.*, [iv], 3, 249—250).—The different processes that have been proposed for the estimation of the alkaloids in coca leaves were compared, and found to yield results which show great divergence. Lyons' process is considered to effect a complete extraction of the alkaloids, but requires 24 hours to carry out. Results almost identical

can be obtained in 2 hours, as follows. Five grams of the powdered leaves are moistened with weak ammonia (2 per cent.), allowed to remain half an hour, then placed in a narrow tubular percolator ($10 \times \frac{1}{2}$ inch), and treated with ammoniated ether until about 100 c.c. has passed through. The ethereal liquid is shaken three times with hydrochloric acid (2 per cent.; about 50 c.c.), the acid extract washed with ether, made alkaline with ammonia, and then extracted three times with ether. The ethereal extract is collected in a weighed porcelain dish, evaporated, and dried at 75°. R. R.

**Detection of Aniline-blue in Bread.** By CHARLES VIOLETTE (*Bull. Soc. Chim.*, 1896, [3], **15**, 456).—A trace of aniline-blue is often employed by bakers to counteract the yellow colour of bread made from oatmeal or inferior flour. A filter paper is placed on a plate and covered with water a few millimetres deep, the suspected bread is crumbled on to the plate, and the filter paper is subsequently examined for blue spots. M. W. T.

**Detection of Coal Tar Colours in White Wines, and their Distinction from Caramel Colours.** By ALBERTO D'AGUIAR and W. DA SILVA (*Compt. rend.*, 1897, **124**, 408—410).—Experiments were made with white wine to which had been added small quantities of dinitronaphthol, chrysoidine, Bismarck brown, orange II, tropeolin, Biebrich scarlet, azoflavin, helianthin, methyl-orange, amidoazobenzene, naphthol-yellow S, or caramel, as the case might be. Sixty c.c. of each wine was made alkaline with ammonia, and agitated with 30 c.c. of amylic alcohol; the latter was separated, filtered, the intensity of the coloration observed, and part of the solution reduced to one-third its original volume, in contact with some threads of silk. In a second series of tests, 5 c.c. of the amylic alcohol solution was evaporated to dryness on a water bath, and the residue was treated with concentrated sulphuric acid to which water was afterwards added. Another set of similar experiments was made, using hydrochloric acid instead of sulphuric. In a third series, the residues, after being heated with concentrated sulphuric acid and water, were filtered, made alkaline with ammonia, again agitated with amylic alcohol, and the second solution thus obtained was treated in the same way as the first.

It was found that caramel scarcely gives any coloration to the amylic alcohol, whilst naphthol-yellow S, the only one of the dyes that gave doubtful results, is readily recognised in other ways. Caramel has practically no dyeing effect on silk, and whilst this is true also of chrysoidine and amidoazobenzene, the latter are readily recognised in other ways. In the tests with sulphuric acid, the results obtained with caramel are very distinct. The general conclusion is, that the amylic alcohol method is not likely to lead to any confusion between coal-tar colours and caramel. C. H. B.

**Reagent for Detecting Albumin and Peptones in the Urine.** By A. JAWOROWSKY (*L'Orosi*, 1896, **19**, 379).—A reagent composed of ammonium molybdate (1 part) and tartaric acid (4 parts) dissolved in water (40 parts), when added to slightly acid urine, gives a whitish precipitate in presence of albumin or peptones, which, in the former

case, is not dissolved by heat, but in the latter dissolves on heating, and separates again on cooling. Most alkaloids are precipitated by this reagent; if these are present, citric acid should be substituted for the tartaric acid used in its preparation, and the urine submitted to a preliminary treatment. This consists in adding excess of sodium carbonate, filtering, evaporating to one third, again filtering, extracting with amylic alcohol, and neutralising with citric acid. W. J. P.

**Estimation of Gluten in Flour.** By BALLAND (*J. Pharm.*, 1896, [6], 4, 250—251).—When flours containing the same percentage of nitrogen are treated by the usual method, they may yield different amounts of gluten. This depends on the sifting and also on the milling process—that is, on the amount of bran which they contain. The estimation of gluten, therefore, whilst supplying a precise method for determining the quality of a flour, is inadequate for determining the amount of nitrogenous substances present, or, in other words, for determining its nutritive value. J. J. S.

**Detection of Tussah in Silk Fabrics.** By F. FILSINGER (*Chem. Zeit.*, 1896, **20**, 324).—After explaining the difficulty of a microscopic investigation, the author calls attention to the fact that, whilst real silk is readily soluble in hydrochloric acid, strong zinc chloride or an alkaline solution of copper-glycerol, tussah silk is scarcely affected by these solvents.

Another peculiarity is that, whilst silk is not readily combustible, tussah silk takes fire much more readily without emitting the unpleasant odour of burning silk. L. DE K.

**Estimation of Lipase.** By MAURICE HANRIOT and L. CAMUS (*Compt. rend.*, 1897, **124**, 235—237).—See this vol., ii, 273.

# General and Physical Chemistry.

**Spectro-chemistry of Nitrogen. V.** By JULIUS W. BRÜHL (*Zeit. physikal. Chem.*, 1897, 22, 373—409).—The author adds to those already published, a large number of observations on the refraction and dispersion of nitrogen compounds. The solids were examined in solution, the solvents employed being ethylic alcohol, acetone, ethylic acetate, benzene, α-bromonaphthalene, ethylic ether, and carbon bisulphide. The sources and the methods of purification of the compounds are given, and the results obtained are shown in the accompanying table, (1) being the molecular refraction for the sodium line, and (2) the dispersion $M\gamma - M\alpha$, calculated according to the Lorenz formula.

| Compound. | 1 | 2 |
|---|---|---|
| Hydrogen nitrate | 10·003 | 0·338 |
| Hydrazine | 8·867 | 0·266 |
| Methylnitramine | 16·79 | 0·76 |
| Isocyanogen tetrabromide | 50·42 | 2·76 |
| as.-Dimethylhydrazine | 18·68 | 0·60 |
| Dimethylnitramine | 21·65 | 0·95 |
| Formodimethylamide | 19·86 | 0·65 |
| Chloroformodimethylamide | 24·88 | 0·77 |
| Methylethylnitramine | 25·82 | 1·07 |
| Thiophen | 24·33 | 1·08 |
| Ethylic sulphide | 28·51 | 0·88 |
| Imidoethylic ether | 24·35 | 0·64 |
| Acetodimethylamide | 24·23 | 0·74 |
| tert.-Butylamine | 24·20 | 0·64 |
| Pyrazine | 22·64 | 1·15 |
| Pyridazine | 22·15 | 0·99 |
| Dimethylfurazan | 23·98 | 0·66 |
| Ethylic methylnitrocarbaminate | 32·26 | 1·13 |
| Butylnitramine | 30·57 | 1·13 |
| sec.-Butylnitramine | 30·48 | 1·10 |
| Methylbutylamine | 28·76 | 0·76 |
| Imidopropyl ethyl ether | 28·76 | 0·75 |
| Diethylic imido-carbonate | 30·53 | 0·77 |
| Methylpyrazine | 27·14 | 1·35 |
| Methylethylfurazan | 28·57 | 0·77 |
| as.-Methylbutylhydrazine | 32·50 | 0·92 |
| Nitropiperidine | 32·93 | 1·26 |
| Methylbutylnitramine | 35·05 | 1·30 |
| Isobutylmethylnitramine | 35·14 | 1·31 |
| Nitrosoethylurethane | 36·33 | — |
| Metabromonitrobenzene | 40·45 | 2·36 |
| Propylpropylideneamine | 32·44 | 0·93 |
| Methylic butylcarbamate | 34·85 | 0·90 |
| Methylic isobutylcarbamate | 34·89 | 0·90 |
| Methylic sec.-butylcarbamate | 34·80 | 0·88 |
| Ethylic dimethyloxamate | 35·70 | 1·06 |
| Propylglyoxalidine | 33·42 | 1·06 |
| Dimethylketazine | 35·98 | 1·41 |
| Methylic butylnitrocarbamate | 41·39 | 1·35 |
| Methylic sec.-butylnitrocarbamate | 41·38 | 1·34 |
| Methylic isobutylnitrocarbamate | 41·38 | 1·34 |
| Ethylic butylnitrocarbamate | 46·08 | 1·45 |
| Ethylic sec.-butylnitrocarbamate | 46·08 | 1·45 |
| Ethylic isobutylnitrocarbamate | 46·07 | 1·47 |
| Hexylnitramine | 39·79 | 1·34 |
| Triformalmethylamine | 38·72 | 1·16 |
| Furylimidoethyl ether | 37·46 | 1·71 |
| Ethylic butylcarbamate | 39·53 | 0·99 |
| Ethylic sec.-butylcarbamate | 39·56 | 0·99 |
| Ethylic isobutylcarbamate | 39·52 | 1·00 |
| γ-Coniceine | 39·22 | 1·06 |
| Isocaproimidoethyl ether | 42·20 | 1·05 |
| Quinoxaline | 40·45 | 3·03 |
| Benzylmethylnitramine | 45·28 | 2·11 |
| Methyl ethyl ketazine | 45·26 | 1·63 |
| Methylmethenylphenyleneamidine | 40·09 | 2·16 |
| Isoquinoline | 41·43 | 2·65 |
| Ethylic hexylcarbamate | 48·84 | 1·22 |
| Toluquinoxaline | 45·31 | 3·44 |
| Triformalethylamine | 52·44 | 1·50 |
| Orthotoluquinoline | 46·62 | 2·98 |
| Metatoluquinoline | 46·77 | 3·02 |
| Paratoluquinoline | 46·88 | 3·03 |
| γ-Methylquinoline | 46·11 | 2·88 |
| α-Methylisoquinoline | 46·03 | 2·85 |
| Kairoline | 48·02 | 2·58 |
| Isoamylideneamine | 51·39 | 1·42 |
| Ethylethenylphenyleneamidine | 49·66 | 2·52 |
| Propylpropenylphenyleneamidine | 59·07 | 2·86 |
| Triformalpropylamine | 66·30 | 1·80 |
| Benzylamine acetoacetate | 66·62 | 4·05 |
| *Solutions.* | | |
| Isocyanogen tetrabromide | 50·82 | 2·91 |
| Nitrourethane | 27·80 | 1·03 |
| Pyrazine | 22·49 | 1·16 |
| Methylglyoxalidine | 24·43 | 0·84 |
| Diethylic chlorimidocarbonate | 35·88 | 1·01 |
| Diethylic bromimidocarbonate | 38·40 | 1·29 |
| Nitrobenzene | 30·01 | 1·17 |
| β-Phenylhydroxylamine | 32·48 | 1·72 |
| Tetramethylethylene nitroso-chloride | (Hγ) 38·33 | |
| Phenylnitramine | 37·95 | 2·87 |
| Parabromophenylnitramine | 46·71 | |
| Orthonitrophenylnitramine | 44·04 | |
| Metanitrophenylnitramine | 44·87 | |
| Paranitrophenylnitramine | 47·36 | |
| Paranitrodiazobenzene methyl ether | 47·76 | |
| Paranitrobenzylnitramine | 48·39 | 3·26 |
| α-Paranitrobenzylnitramine(–N–)-methy ether | 53·09 | 3·41 |
| β-Paranitrobenzylnitramine(–O–)-methy ether | 53·99 | 3·42 |
| Paranitrobenzylisonitramine methyl ether | 53·52 | 2·88 |
| α-Benzylamine acetoacetate | 67·90 | 4·37 |
| β-Benzylamine acetoacetate | 67·78 | 4·37 |
| α-Dibenzylnitrosohydroxylamine | 70·77 | |
| β-Dibenzylnitrosohydroxylamine | 71·02 | 3·54 |
| Benzylaminoethylic cinnamate | 87·52 | 5·91 |

L. M. J.

**Apparatus for Examining the Spectra of Gases.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1897, **124**, 525—528).—The author describes an apparatus for facilitating the examination of the spectra of gases under atmospheric pressure. Although inferior to the ordinary Plucker tubes as regards definition of the lines, the simplicity of construction and ease of manipulation make it possible to include an examination of the spectrum in the ordinary qualitative analysis of a gas. The apparatus consists of a straight glass tube, 10 to 12 cm. long and 7 to 15 mm. broad, closed at one end, into which a platinum wire is fused. A second and much narrower tube is bent in the form of a V, and has a platinum wire running through its whole length, and projecting at both ends. At one end, which serves as one of the poles for the electric discharge, the glass is fused round the wire; the other end can be connected with the coil. The sealed limb of the second tube is fitted into the first tube by means of a cork, in such a way that it can slide up and down, so that the distance between the two platinum wires can be adjusted. A short capillary tube must also pass through the cork, or there must be a notch in its side to allow for the expansion due to the sparks. The straight tube is filled with mercury, placed in a small mercury trough, and a small quantity of the gas to be examined is passed into it. The bent tube is now slipped up into it, and the cork fitted into its place. A condensed or uncondensed spark is passed between the platinum wires, the distance between them being adjusted to give the best result. The discharge should be frequently interrupted, and a condensed spark should be avoided if possible. C. H. B.

**Unknown Lines observed in the Spectra of certain Minerals.** By J. NORMAN LOCKYER (*Proc. Roy. Soc.*, 1896, **60**, 133—140).—Photographs of the spectra, at atmospheric pressure, of the following gases, which from experience are likely to be associated with those given off by minerals, have been obtained, and the lines tabulated:—Nitrogen, oxygen, chlorine, carbonic anhydride, coal gas, sulphuric anhydride, phosphoretted hydrogen, and argon. The lines of mercury, potassium, and platinum have also been photographed, the latter because they are always present in the spectra, for the reason that the spark is passed through platinum poles, whilst the lines of mercury and potassium frequently occur, according as the gases are collected over mercury or potash.

A list of the lines obtained for the gas from eliasite is given, after eliminating the lines due to the old gases. The wave-lengths of several of the former lines approach very near those of the latter.

Attempts have been made to concentrate the eliasite gas, but the quantity is so small, and so largely admixed with helium and argon that a new research with larger amounts of material is essential.

A complete list of the unknown lines so far noticed in other minerals is also given, together with the facts as to whether or not lines nearly coincident in position have been observed in any celestial body.

A. W. C.

**Spectrum of Cyanogen as Produced and Modified by Spark Discharges.** By W. NOEL HARTLEY (*Proc. Roy. Soc.*, 1896, **60**, 216—221).—The chief evidence of the existence of a cyanogen spectrum

is that this substance is actually synthesised in the arc when nitrogen is present; that without nitrogen elementary carbon does not yield the same spectrum; that cyanogen gas burns with a flame of which the banded spectrum is known as that of cyanogen by reason of the foregoing facts; and, lastly, that when a condensed spark is passed between electrodes of gold in an atmosphere of cyanogen, the same spectrum can be photographed.

Facts are recorded which lend support to the view that the flame of burning cyanogen ought to exhibit the spectrum of carbon.

The author considers that the facts derived solely from observations on the arc are insufficient to establish the existence of a definite cyanogen spectrum. Moreover, it has been shown that lines somewhat resembling the edges of the cyanogen bands are seen when graphite poles are moistened with water and the spark passed through air; if the water contains the chlorides of ammonium, calcium, or zinc, the lines are intensified and develop into bands which become stronger with concentration of the solution; the explanation of this is that the only mineral acid free from ammonia is freshly made sulphurous acid. Salts of calcium or zinc prepared from ordinary mineral acids always contain ammonium salts; hence, if the bands said to be cyanogen bands are due to the nitrogen of the ammonia, the spectrum of the graphite poles will exhibit bands more strongly, as the solution used is more concentrated.

That the bands and lines are really due to cyanogen and not to elementary carbon is proved by the following facts.

The lines belonging to the edges of the bands in the spectra of a flame of cyanogen were found to coincide exactly with those photographed from a potassium cyanide solution, when the spark was passed in an atmosphere of carbonic anhydride or cyanogen; or when the spark was passed between gold electrodes in cyanogen gas.

The cyanogen spectrum in the flame of burning cyanogen is accounted for because there is excess of the gas present and the temperature of the flame is exceedingly high, but the gas within it is not in contact with a solid substance, hence immediate decomposition does not occur, and the gaseous compound is only heated to incandescence.

A. W. C.

**Birotation of Glucose.** By HEINRICH TREY (*Zeit. physikal. Chem.*, 1897, 22, 424—463).—The author had previously investigated the effect of acids on the birotation of aqueous and alcoholic solutions of glucose and glucose anhydride (Abstr., 1896, ii, 139), and the observations are here extended to the effect of various salts and of other solvents. Sodium sulphate and acetate, potassium nitrate and iodide, ammonium chloride and thiocyanate, barium chloride, magnesium sulphate and chloride, aluminium chloride, lead acetate, mercuric chloride, and cadmium iodide all caused in N/20 solutions an acceleration of the retrogression, that due to the magnesium salts being most marked. Sodium chloride alone of all the salts examined has a retarding influence (compare Levy, Abstr., 1895, i, 586). In methylic alcohol solution, cadmium iodide produced a marked increase, and potassium iodide a slight increase of velocity, the final value being only slightly different from that of a pure alcoholic solution. By

increasing the concentration of the salts, however, the acceleration can be changed to a retardation. The effect of alkaline solutions was investigated, and with sodium hydroxide the ordinary limit of about 50° is almost immediately obtained, but the value does not remain constant, as it further diminishes and may attain zero or even a negative value. Sodium carbonate gives a constant value of about 50° very speedily, whilst ammonia and potassium cyanide cause a further decrease below this value. The effect here appears to be due to the presence of hydroxyl ions, for the measurement of which the author considers the reaction very convenient. The accelerative effect of sulphuric acid is diminished by the addition of sodium sulphate, that of hydrochloric acid, however, being increased by the addition of sodium chloride, and also by the addition of alcohol. Acetic and propionic acids cause a decrease, cacodylic acid an increase, of velocity, and neutral compounds such as cane-sugar appear to have a slight retarding effect. Multirotation also occurs in acetone solutions, the behaviour being very similar to that of solutions in methylic and ethylic alcohols. Measurements were also made of the internal friction of aqueous and alcoholic solutions of the anhydride and hydrate, the values being slightly different for the two compounds. L. M. J.

**Theory of Accumulators.** By Karl Elbs (*Zeit. Elektrochem.*, 1896, 3, 70).—The source of the electromotive force of a secondary battery is to be found, according to Le Blanc, in the change of quadrivalent into bivalent lead ions; whereas, Liebenoff and Löb assume the presence of the ion $\overset{-\,-}{PbO_2}$ in the solution, which, on abandoning its charge, is deposited as lead peroxide. The author is led, by his observations on the electrolysis of solutions of the acetates, to support the first view. The acetates are divided into three groups: (1) Those yielding, at the anode, mainly ethane and carbonic anhydride; (2) those yielding mainly oxygen; (3) those from which no gas is evolved. Group (1) includes the acetates of metals of constant valency; group (2) contains the acetates of metals which are bi- or trivalent, and whose higher oxide yields less stable salts than the lower; group (3) contains metals of valency between two and four which form comparatively stable peroxides. In the last two groups, it is supposed that the $CH_3 \cdot CO_2$ group liberated at the anode combines with the salt in the solution to form the acetate of the higher oxide. These salts are readily decomposed by water; cobalt triacetate, for example, would give cobalt acetate, acetic acid, and oxygen, whilst lead tetracetate yields acetic acid and lead peroxide. From this point of view, the formation of lead peroxide in an accumulator is preceded by the formation of the salt, $Pb(SO_4)_2$, containing quadrivalent lead. T. E.

**Theory of Accumulators.** By Walther Löb (*Zeit. Elektrochem.*, 1896, 3, 100).—According to the views put forward by Elbs (preceding abstract) equivalent quantities of lead and lead peroxide should separate at the electrodes when a solution of lead acetate is electrolysed. The author's experiments show that this is not in general the case; by using a large anode, the greater part of the lead may be deposited as peroxide. To explain this anomaly, Elbs supposes that lead tetracetate diffuses from the anode to the cathode, and there dissolves the lead.

The author rejects this explanation, because if lead tetractate were distributed through the whole solution, lead peroxide should not separate only at the anode. [Even if lead tetracetate acted in the way supposed by Elbs, equivalent quantities of lead and lead peroxide would be found, only they would not be equivalent to the quantity of electricity passed through the cell.—ABSTRACTOR].

The author thinks that the phenomena are most readily explained by supposing that the solution contains the ion $\bar{Pb}\bar{O}_2$, which need be present only in very small quantity, and which may be produced by the hydrolytic decomposition of the lead salt. T. E.

**Action of Hydrochloric Acid on Metallic Sodium at Low Temperatures.** By ERNST DORN and B. VÖLLMER (*Ann. Phys. Chem.*, 1897, [ii], 60, 468—477).—Pictet's observation that hydrochloric acid is without action on metallic sodium at $-80°$, led the authors to a further examination of the behaviour of hydrochloric acid at low temperatures. The acid used had a specific gravity of 1·1211 at 18°, and therefore contained 24·3 per cent. HCl. The electrical conductivity of this acid was found to decrease with falling temperature until, at $-82·2°$, the conductivity was only about $\frac{1}{35}$th of that at 18°; the conductivity curve is given by the following equation: $\nu = 10^{-8}[5065·0 + 95·753t + 0·2706t^2 - 0·002084t^3]$. The decrease in conductivity appears to be mainly due to the increase in viscocity, as the viscosity at $-80°$ is found to be about 55 times greater than that at 18°. The density of the solution was measured at $-16°$, and found to be 1·137 and again at $-78·4°$, when the value 1·174 was obtained. The E.M.F. of the combination Na | HCl | Pt is 3·018 volts. at $-80°$, the solution pressure of sodium is, therefore, still very considerable at $-80°$. This suggests that the chemical action of sodium on hydrochloric acid does not entirely cease, but is merely retarded at the above temperature. Examination of the solution showed that, as a matter of fact, sodium chloride is produced in appreciable quantity, and that action is retarded, but not completely stopped. H. C.

**Specific Gravity and Electrical Conductivity of Normal Solutions of Sodium and Potassium Hydroxides, and of Hydrochloric, Sulphuric, Nitric, and Oxalic Acids.** By E. H. LOOMIS (*Ann. Phys. Chem.*, 1897, [ii], 60, 547—551).—The following table contains the specific gravities and the electrical conductivities in mercury units of the solutions examined:

| | Sp. gr. 18°/4°. | $K \times 10^7$ at 18°. |
|---|---|---|
| NaOH | 1·0418 | 145 |
| KOH | 1·0481 | 170 |
| HCl | 1·0165 | 279 |
| $HNO_3$ | 1·0324 | $278_5$ |
| $\frac{1}{2}H_2SO_4$ | 1·0306 | 183 |
| $\frac{1}{2}C_2H_2O_4$ | 1·0199 | 55 |

H. C.

**Electrolytic Conductivity of Solid Substances.** By CARL FRITSCH (*Ann. Phys. Chem.*, 1897, [ii], 60, 300—313).—The author has determined the conductivity of a number of solid substances, taken either in the form of precipitates or compressed plates, and further

examined the effect which the addition of small quantities of a foreign solid has on the conductivity of the pure solid under examination. The effect of the addition of small quantities of a second salt to that which is under examination is in nearly all cases to largely increase the electrolytic conductivity of the latter; this would appear to be best explained by assuming the formation of a solid solution, in which the solvent, lead chloride, for example, causes ionisation of the dissolved salt, say potassium chloride. It is not impossible that the conductivity of the solid salts themselves is caused by the presence of traces of impurities, but this point would require specially investigating in each case. The conductivity increases rapidly with rising temperature, but the changes in the temperature coefficients are much smaller than those in the conductivities themselves. H. C.

**The Number of Ions in some Ammonia Cobalt Compounds.** By EMIL PETERSEN (*Zeit. physikal. Chem.*, 1897, 22, 410—423).—Werner and Miolati, in their determinations of the ions in ammoniacal cobalt compounds (this vol., ii, 100), took into account only the molecular conductivity, whereas observations on the osmotic pressure are also necessary. The author has therefore determined both freezing point depression and molecular conductivity at 0° and various concentrations. From the molecular depression, by division by 18·7, the Van't Hoff coefficient, $i$, is obtained, and hence the number of ions, $k$, can be calculated from the equation $i = 1 + (k-1)\alpha$ where $\alpha$ is the degree of dissociation. Dinitrotriamminocobalt chloride is thus found to form three ions, the nitrite, however, being undissociated, the latter result being in agreement with Werner's views. Dinitrotetramminocobalt nitrate forms four ions, a similar result being obtained for dichlorotetramminocobalt chloride and nitrate, dibromethylenediamminocobalt nitrate, dichlorethylenediamminocobalt chloride and nitrate, and for the chloronitrotetramminocobalt chloride; the dichlorethylenediamminocobalt bromide differing from the other praseo-salts by only forming three ions. The author does not consider, however, that these results, which indicate only the number, justify speculations on the nature of the ions. L. M. J.

**Measurement of Great Electrolytic Resistances with a Constant Current.** By R. MALMSTRÖM (*Zeit. physikal. Chem.*, 1897, 22, 331—335).—The method suggested by Wilderman (Abstr., 1894, ii, 375) for the determination of electrolytic resistance is open to several practical objections, notably the difficulty of obtaining a sufficiently high constant electromotic force. The author has, therefore, examined the method suggested by Nernst (Abstr., 1894, ii, 437) and finds for resistances of 1000 ohms and upwards it is accurate and convenient, and preferable to either the ordinary Kohlrausch method or to that adopted by Wilderman. L. M. J.

**Colours Produced by the Cathode Discharge in some Salts.** By EUGEN GOLDSTEIN (*Ann. Phys. Chem.*, 1897, [ii], 60, 491—499).—In a former paper (Abstr., 1895, ii, 150), the author recorded certain remarkable colour changes which salts undergo when under the influence of the cathode discharge. These changes were regarded as fairly permanent if the salt was preserved in a vacuum, but a further

series of observations have been made on this point. From these it appears that the coloured salt loses its colour again in a short time under the influence of light, but that in the dark it can be preserved for an indefinite time without undergoing change. The change under the influence of light is so marked and rapid that these coloured salts must be regarded as some of the most sensitive compounds known. The action of light is hastened and assisted by that of heat.

H. C.

**Electrical Anomaly and Chemical Constitution.** By PAUL DRUDE (*Ann. Phys. Chem.*, 1897, [ii], **60**, 500—509).—Certain liquids are found to possess an anomalous absorption for rapid electrical vibrations and an anomalous dispersion of their electrical indices of refraction (ratio of the wave-length of the vibration in air to that in the compound under investigation). This anomalous absorption appears to be intimately connected with chemical constitution, for the hydrocarbons, the ethers, the ketones, and aldehydes behave normally, but alcohols and acids, and generally compounds containing the hydroxyl group, possess an anomalous absorption. The differences are so marked that in many cases this property would probably be of service in settling vexed questions of constitution. An examination of ethylic acetoacetate, for example, shows that, as this compound possesses a normal behaviour, it cannot be regarded as containing the hydroxyl group. Ethylic aceto-oxalate, on the other hand, appears from the results obtained to contain hydroxyl. An exception to the above rule appears in the case of water, the behaviour of which is perfectly normal. Where an anomalous behaviour is noticed for the liquid, this appears to be maintained also by the compound in the solid state.

H. C.

**Chemical Action of Electrical Oscillations.** By ALEXANDER DE HEMPTINNE (*Zeit. physikal. Chem.*, 1897, **22**, 360—372).—The apparatus employed for the production of the oscillations was similar to that of Lecher (*Ann. Phys. Chem.*, 1890, [ii], **41**, 850), and allowed of the ready alteration of the wave-length. A Wimshurst machine driven at constant speed by a motor was employed in most cases, but where greater tension was required, a Tesla transformer was used. Researches with ammonia at pressures of 5 mm., 15 mm., and 50 mm. showed that the velocity of decomposition decreases with increasing pressure, and a maximum was obtained in each case some time after the commencement of the decomposition, after which it decreased, indicating a final equilibrium. The velocity is also markedly influenced by the energy of the discharge. The percentage of ammonia finally decomposed varies with the pressure, being about 50 per cent. at 49 mm. and 95 per cent. at 20 mm., but the values do not agree with the expression $p_3^2 = kp_1 p_2^3$, which should theoretically obtain in the case of a heat dissociation. The decomposition is further lowered by the addition of nitrogen or hydrogen, the latter having, as expected, the greater effect, but the quantitative results are not in accord with theoretical deductions. Under the influence of electrical oscillations, nitrogen and hydrogen combine to the extent of 3 or 4 per cent., the final quantity being apparently almost independent of the pressure. In all these cases, no action occurs unless the tube containing the gas becomes luminous; and it was

observed that one tube may screen another, so that if two tubes at slightly different pressures be placed between the plates and the discharge adjusted so that only one tube lightens, a slight increase of pressure in this tube causes it to become dark, and the second tube to lighten and be decomposed. Carbon bisulphide is also decomposed, the velocity being well represented by the equation $dx/dt = k(a - x)$. Some thick liquids, such as glycerol, exhibit an increase of vapour pressure when exposed to the action of the oscillations, a similar effect occurring with oxalic acid, whilst calcium chloride appears to be entirely unaffected. L. M. J.

**The Melting Points of some Organic Compounds.** By BERNHARD VON SCHNEIDER (*Zeit. physikal. Chem.*, 1897, **22**, 225—236).—The author adds a large number of melting point determinations to those previously published (Abstr., 1896, ii, 290). The values for anisoil and phenetoil were obtained as −37·8° and −33·5°, although Haase states that they become gelatinous at −75°, and the author further considers several of Haase's determinations to be too low, probably owing to the use of a capillary tube. Henry's law regarding the rise and fall of the melting points of the ethereal salts of the oxalic series was found to hold for both methylic and ethylic salts, a similar relationship obtaining in the case of the chloro- and bromo-derivatives of acetic acid and the corresponding amides, as well as for the chloroderivatives of benzene and toluene. Dewar (Roy. Inst., Jan., 1894), classes turpentine, ethylic nitrate, and quinoline among compounds which form glassy masses, but the author found they solidified as crystalline masses at the temperatures −65°, −112°, and −19·5° respectively. He, however, finds, like Dewar, that some compounds solidify to glassy masses. The author further verifies Petersen's conclusion, that chlorocompounds have a lower melting point than bromo-compounds, and these lower than the iodo-compounds; also that the chlorides melt at lower temperatures than the corresponding cyanides. The determinations are as follows:—diethylic oxalate, −41°; ethylenic dichloride, −36°; ethylenic chlorobromide, −16·6°; ethylenic chloriodide, −15·6°; chlorobenzene, −45°, bromobenzene, −30·5°, iodobenzene, −28·5°; benzonitrile, −12·9°; diethylaniline, −38·8°; paraphenetidine, +2·4°; orthonitrotoluene, −14·8°; anisoil, −37·8°, ethylthiocarbimide, −5·9°; chlorpicrin, −69·2°; ethylic salicylate, +1·3°; ethylic chloride, −142·5°; ethylic bromide, −125·5°; ethylic iodide, −118°; ethylidenic chloride, −101·5°; ethylic nitrate, −112°; propionitrile, −103·5°; diethylic malonate, −49·8°; diethylic succinate, −20·8°; benzylic cyanide, −24·6°; methylic salicylate, −8·3°; phenetoil, −33·5°; butyric acid, −7·9°; propionic acid, −22°; benzylic chloride, −43·2°, benzylidenic chloride, −16·1°; benzotrichloride, −21·2°; phenylthiocarbimide, −21°; orthanisidine, +5·2°; acetonitrile, −44·4°. A few compounds changed to glassy masses at below −80°. L. M. J.

**Determination of Freezing Points.** By J. A. HARKER (*Proc. Roy. Soc.*, 1896, **60**, 154—156).—The methods at present in use for the determination of the freezing point are unsatisfactory, and cannot be depended on to more than 0·001° to 0·002°. The author describes a method, consisting essentially of cooling the liquid to slightly below

its freezing point, dropping in a crystal of the solid, and observing the temperature with the aid of a modified platinum thermometer. By this means more consistent results, agreeing to within one or two ten-thousandths of a degree, may be obtained. A. W. C.

**Former Determinations of Freezing Points.** By LOUIS C. DE COPPET (*Zeit. physikal. Chem.*, 1897, **22**, 239—240).—The author, considering his determinations of freezing points (1871) of saturated solutions to be comparatively unknown, republishes the numbers, which are given below, together with the weight of anhydrous salt per 100 parts of water:—KCl, $-11\cdot1°$, 24·6; NaCl, $-21\cdot8°$, 29·6; $NH_4Cl$, $-15\cdot8°$, 22·9; $SrCl_2$, $-18\cdot7°$, —; $BaCl_2 + 2H_2O$, $-7\cdot8°$, 25·1; $ZnSO_4 + 7H_2O$, $-6\cdot5°$, 37·3; $CuSO_4 + 5H_2O$, $-1\cdot6°$, 13·5; $(NH_4)_2SO_4$ $-19\cdot05°$, 62·2; $K_2CrO_4$, $-11\cdot3°$, 57·7; $Na_2SO_4 + 10H_2O$, $-1\cdot2°$, 4·0; $Na_2SO_4 + 7H_2O$, $-3\cdot5°$, 14·5; $Na_2CO_3 + 10H_2O$, $-2\cdot1°$, 5·3; $KNO_3$, $-2\cdot85°$, 10·7; $NaNO_3$, $-18\cdot5°$, 58·5; $NH_4NO_3$, $-17\cdot3°$, 70·0; $Ba(NO_3)_2$, $-0\cdot7°$, 4·5; $Sr(NO_3)_2$, $-5\cdot7°$, 32·4; $Pb(NO_3)_2$, $-2\cdot7°$, 35·2. L. M. J.

**Freezing Points of Dilute Aqueous Solutions. III.** By E. H. LOOMIS (*Ann. Phys. Chem.*, 1897, [ii], **60**, 523—546. Compare Abstr., 1896, ii, 352).—The author has continued his researches on the freezing points of dilute aqueous solutions, and in the results here brought forward claims an accuracy to within 0·0005°. Solutions of the chlorides of lithium, calcium, and strontium give molecular depressions, which at first decrease with rising dilution, and after attaining a minimum value again increase. Stannic chloride in the most dilute solution examined gives a molecular reduction of 126·1. As a compound containing five ions could not give, even on complete electrolytic dissociation, a greater reduction than 94·5, the author concludes that stannic chloride decomposes in aqueous solution, and perhaps forms $SnCl_2$ and 2HCl. The behaviour of phosphoric acid, which gives a molecular reduction of 28·2 in the most dilute solution examined, is taken as indicating that this compound dissociates into the ions H and $H_2PO_4$. In keeping with this, it appears that $KH_2PO_4$ also dissociates into the two ions K and $H_2PO_4$, but the behaviour of $Na_2HPO_4$ is best explained by its dissociation into the *three* ions, Na, Na, and $HPO_4$; and $Na_3PO_4$ from the cryoscopic results must be regarded as dissociated into *four* ions. Sodium silicate, $Na_2SiO_3$, like stannic chloride, gives a much greater molecular depression than would accord with the dissociation hypothesis. The organic acids, acetic, oxalic, succinic, tartaric, and citric, all behave as electrolytes, and not as non-electrolytes. Acetic acid, in its more concentrated solutions, acts, however, as a non-electrolyte, the molecular depression increasing regularly with the concentration. A comparison of the results obtained with the values deduced from the Van't Hoff and Arrhenius theories shows that there is a complete accordance for the chlorides of lithium and calcium. A satisfactory agreement is obtained with acetic, tartaric, and citric acids, and the agreement is also fair in the case of strontium chloride. On the other hand, the values for $HNO_3$, KOH, and NaOH do not agree with those demanded by the dissociation hypothesis, differences of from 8 to 11 per cent. being obtained in the

most dilute solutions. The differences are, curiously enough, less for the more concentrated solutions. H. C.

**Aniline in Cryoscopy.** By G. Ampola and C. Rimatori (*Gazzetta*, 1897, **27**, i, 35—51).—The authors have made series of determinations of the depressions of the freezing point of aniline by bromobenzene, bromotoluene, nitrobenzene, chloroform, bromoform, ethylenic bromide, benzene, toluene, paraxylene, thiophen, benzaldehyde, ethylic oxalate, pyridine, piperidine, dimethylaniline, quinoline, ortho- and paratoluidine, coniine, valeric acid, isobutyric acid, phenol, cresol, carvacrol, thymol, methylic alcohol, ethylic alcohol, caprylic alcohol, benzylic alcohol, isobutyric alcohol, and the diethylic ether of glycerol. The molecular depression calculated as the mean from those cases in which the behaviour is most regular is 58·67, whilst the value calculated by Raoult's rule is 57·66.

Aniline differs considerably from dimethylaniline as a solvent in cryoscopy (compare following abstract) in that its behaviour is more like that of acid solvents such as acetic acid; compounds containing hydroxyl give molecular depressions in aniline which do not appreciably differ from those given by compounds containing no hydroxyl. This analogy of behaviour also extends to fairly concentrated solutions, excepting in the case of aniline solutions of methylic, ethylic, and isobutyric alcohols, when greater deviations than usual from the law are observed. Ethylenic bromide and benzaldehyde behave abnormally, owing probably to their combining with the solvent. W. J. P.

**Dimethylaniline in Cryoscopy.** By G. Ampola and C. Rimatori (*Gazzetta*, 1897, **27**, i, 51—68).—The authors have determined the depressions of the freezing point of dimethylaniline caused by benzene, toluene, paraxylene, thiophen, bromotoluene, chloroform, bromoform, benzaldehyde, nitrobenzene, bromobenzene, bromotoluene, veratrol, ethylic oxalate, ethylenic bromide, methylic alcohol, isobutylic alcohol, trimethylcarbinol, benzylic alcohol, caprylic alcohol, the diethylic ether of glycerol, pyridine, piperidine, aniline, quinoline, orthotoluidine, formic acid, isobutyric acid, valeric acid, phenol, paracresol, thymol, and carvacrol. The mean molecular depression of the freezing point of dimethylaniline calculated from the most suitable of the above determinations is 58, whilst that calculated by Raoult's rule is 75·02.

Most substances behave fairly regularly in dimethylaniline solution, and as a solvent this base resembles the hydrocarbons and their halogen derivatives. The molecular depression of the freezing point caused by the alcohols is nearly normal in dilute solutions and diminishes rapidly as the concentration increases, being only 7 in a 25 per cent. solution of methylic alcohol in dimethylaniline. Phenol and paracresol give low molecular depressions, which diminish as the concentration increases although not so rapidly as in the case of the alcohols; thymol, carvacrol, and the alkaloids show fairly normal behaviour. Formic acid behaves much like methylic alcohol, and the acids generally behave more regularly as their molecular weights rise. The hydrocarbons, ethers, and aldehydes give molecular depressions greater than the normal in dilute solution, and as the concentration increases the molecular depressions assume less than the normal value. W. J. P.

**Calculation of Heats of Dissociation and Combination Based on a Theory of Valency and Affinity.** By JOACHIM SPERBER (*Zeit. anorg. Chem.*, 1897, 14, 164—171).—Upon certain speculations with reference to valency and affinity, the author bases calculations of the heats of dissociation and combination of some of the elements. The heat of dissociation of chlorine is given as 44 Cal., and the heat of combination of hydrogen with chlorine as 66 Cal. The heat of dissociation of an equivalent of oxygen is calculated as 83·9 Cal., and the heat of combination of an equivalent of oxygen with hydrogen as 112·7 Cal. H. C.

**Change of Free Energy in the Formation of Insoluble Mercury Compounds.** By STEFAN BUGARSZKY (*Zeit. anorg. Chem.*, 1897, 14, 145—163).—By measuring the E.M.F. of certain cells, in which mercurous salts react with soluble electrolytes producing insoluble mercurous compounds, the author determines the change of free energy in the reactions. This is compared with the total energy change, the results obtained, given in heat units, being as follows:

| Reaction. | Total energy. | Free energy. |
|---|---|---|
| $HgCl + KBr$ | 4010 cal. | 2971 cal. |
| $HgC_2H_3O_2 + KBr$ | 12000 ,, | 6906 ,, |
| $HgCl + KI$ (yellow iodide) | 9310 ,, | 7134 ,, |
| $HgCl + KI$ (greenish-yellow iodide) | 9160 ,, | 7127 ,, |
| $HgC_2H_3O_2 + KI$ | 17275 ,, | 9883 ,, |
| $2HgCl + 2KOH$ | – 3280 ,, | 7566 ,, |
| $2HgC_2H_3O_2 + 2KOH$ | 13270 ,, | 12138 ,, |
| $Hg_2SO_4 + 2KCl$ | 23330 ,, | 13940 ,, |
| $2HgCl + 2KSH$ | 23550 ,, | 41348 ,, |
| $HgNO_3 + KCl$ | 12160 ,, | 6930 ,, |

The soluble electrolytes were employed in centinormal solution.

H. C.

**Absolute Determination of the Expansion of Water.** By MAX THIESEN, KARL SCHEEL, and H. DIESSELHORST (*Ann. Phys. Chem.*, 1897, [ii], 60, 340—349).—The principle of the method adopted by Regnault for the determination of the expansion of mercury, that of measuring the heights of two communicating and counterbalancing columns of the liquid maintained at different temperatures, was adopted for the determination of the expansion of water. The results obtained for the densities and volumes at different temperatures, referred to those at the point of maximum density, were as follows:

| Temperature. | Density. | Volume. |
|---|---|---|
| 0° | 0·9998679 | 1·0001321 |
| 3·98 | 1·0000000 | 1·0000000 |
| 10 | 0·9997272 | 1·0002728 |
| 15 | 0·9991263 | 1·0008745 |
| 20 | 0·9982298 | 1·0017733 |
| 25 | 0·9970714 | 1·0029372 |
| 30 | 0·9956732 | 1·0033456 |
| 35 | 0·9940576 | 1·0059779 |
| 40 | 0·9922417 | 1·0078190 |

The temperatures are those of the hydrogen thermometer. H. C.

**Internal Friction of Salt Solutions and Mixtures.** By Aristides Kanitz (*Zeit. physikal. Chem.*, 1897, **22**, 336—357).—The internal friction was determined in the case of a large number of salt solutions, Ostwald's form of apparatus being employed. According to Arrhenius, the effect of dilution is given by the expression $H = A^x B^y$, where $H$ is the friction of the mixture, $A$ and $B$ that of the components, and $x$ and $y$ their respective volumes. This equation is first tested for a number of single salts, namely, solutions of ammonia, ammonium chloride, ammonium nitrate, ammonium sulphate, potassium hydroxide, potassium carbonate, potassium dichromate, sodium hydroxide, sodium carbonate, ferric chloride, and dichloracetic acid, the concentration varying from 2N to N/8. The observed and calculated values agree well in most cases, but the values are throughout little removed from unity. The difference between the friction coefficients of the hydroxide and chloride is much less in the case of the ammonium than of the potassium salts, a result attributed to the slight dissociation of the ammonium hydroxide. The difference, however, in the case of the quaternary amines is approximately equal to that of the potassium compounds. In the amines, the friction increases with the addition of methyl or ethyl groups, except in the case of the change from the trimethyl- to tetramethyl-ammonium chloride. A large number of salt solutions were also examined; Arrhenius' formula giving on the whole results in accordance with the observations. In some cases, differences may be ascribed to dissociation changes consequent on the mixtures of the solutions; in others, to the formation of double salts, as in many solutions containing mercuric chloride. The friction in the case of ferric chloride is very great, and is probably due to hydrolytic decomposition and the formation of colloidal solutions, hence by the additions the friction is considerably less than that calculated. Molecular complexes are also probably formed in the case of mixtures of potassium or sodium and lead nitrate, or potassium or sodium and strontium nitrates, results also in accordance with previous work of Le Blanc and Noyes (Abstr., 1891, 388).

L. M. J.

**The Formation and Changes of Solids.** By Wilhelm Ostwald (*Zeit. physikal. Chem.*, 1897, **22**, 289—330).—The author first considers the solidification of overcooled melted solids and the crystallisation of supersaturated solutions, and endeavours to determine the least amount of solid which can bring about the change. Salol (melting point 39·5°) was found very convenient for the purpose, as it may be kept overcooled for weeks, although a hair, or filament of glass, that has been drawn lightly across a crystal can effect the solidification of the liquid. The hair or glass may, however, be "sterilised" by drawing a few times between the fingers, or more certainly by heating to 40°. By well mixing the salol with nine times its weight of an inactive compound, such as quartz powder, and repeating this process, the solid may be "diluted" to any desired extent, and it was found that, if freshly prepared, this dilution has to be done six times before the solid loses its specific power; but on standing for two days the D.4 was also found incapable of effecting the solidification, that is, had lost the properties of solid salol. This may be due to the salol no longer being present in the

solid state, but in the gaseous form condensed upon the surface of the diluting solid, and analogous results were obtained in other cases. The author gives to the above form of instability, where the change to solid can only be caused by the presence of the solid itself, the name of "metastabile," the term labile being applied to those cases where other causes may effect the solidification, as in the case of most liquids cooled much below the melting point. The general law is stated that, during a transition from a particular state to one of greater stability, the change is not necessarily to the most stable but to the nearest. This law is illustrated by a large number of examples, such as the solidification of melted sulphur to the monoclinic and not the rhombic form, the changes of mercuric iodide, the formation of liquid drops of benzoic and other acids when precipitated by mineral acids, the production of potassium chloride and hypochlorite by the action of chlorine on potassium hydroxide, &c. The crystallisation of a supersaturated solution of sodium chlorate is more fully examined, and it is found that moisture or an unsaturated solution lowered the activity of the diluted crystals; but this was not the case with a saturated or supersaturated solution. A method of observation analogous to the 'culture' method of bacteriology is described, by which the limiting quantity of salt capable of effecting the solidification was obtained as $0{\cdot}6 \times 10^{-10}$. Similar work with alums, sodium potassium tartrate, borax, and barium chloride is recorded, the necessary dilution of the solid and the time elapsing before crystallisation being found to vary greatly. The capability of effecting crystallisation is, the author considers, a most convenient and certain test for isomorphism; thus, overcooled melted metachloronitrobenzene solidifies on the addition of metabromonitrobenzene, but not on the addition of either the parachloro- or parabromo-compound. L. M. J.

**Inflammability of Explosive Mixtures of Gases.** By FRIEDRICH EMICH (*Monatsh.*, 1897, 18, 6—26).—When the mixture of hydrogen and oxygen obtained by the electrolysis of water is exploded, a small residue always escapes combustion; this probably existed as a layer coating the walls of the vessel, by which it was so far cooled that the explosion was no longer propagated in it. In order to obtain an approximate estimation of the thickness of this layer, electrodes were constructed consisting of pointed aluminium (or platinum) wires of 1 mm. diameter enclosed in glass capillary tubes, the ends of which were ground flat so that the terminal points of the wires lay in the centre of the plane glass surfaces thus produced. These electrodes were placed opposite each other, and so as to penetrate vertically the walls of a horizontal thick glass tube; the lower electrode was cemented in the wall, the upper could be moved up and down through a stuffing-box by means of a micrometer screw. The horizontal tube having been filled with the gaseous mixture, the upper electrode was made to touch the lower one; it was then screwed back a little at a time, and at each resting-place a spark was passed. At first, the very short sparks obtained were unable to bring about an explosion of the gas; as soon as an explosion occurred, the distance apart of the electrodes was noted, and this was taken as the length of the shortest spark that

would produce an explosion of the mixture in question. With electrodes of 5·5 mm. diameter, this length was 0·22 mm. in a mixture of 2 vols. of hydrogen with 1 vol. of oxygen under normal conditions; and since the distance apart of the two flat surfaces of the electrodes was small in comparison with the dimensions of the surfaces, this distance may be taken as the thickness of the layer in which the explosion can only just propagate itself. This distance is independent of the metal of the electrode; with electrodes of smaller diameter (2·0 mm.), it is found to be slightly less, but a diameter of 2·7 mm. suffices to give the same result as one of 5·5 mm.

The more easily inflammable a gaseous mixture is, the shorter will be the spark that is just able to explode it. Defining inflammability in this way as inversely proportional to the minimum length of spark necessary for explosion, it is found that, with mixtures of hydrogen and oxygen in the proportions of 2 : 1 and 1 : 1 by volume, and under pressures varying from 730 mm. to 156 mm., the inflammability is nearly proportional to the pressure, but increases rather more rapidly. The effect of temperature is small; an increase from the ordinary temperature to 380° only increases the inflammability by $\frac{1}{7}$th.

It is found that dilution of the electrolytic mixture of hydrogen and oxygen (2 : 1 by volume) with oxygen actually increases the inflammability, the maximum inflammability being attained when the gases are present in equal proportions by volume. Dilution with hydrogen, nitrogen, or carbonic anhydride at first occasions a slight increase of inflammability, and finally a decrease, comparison being made with pure electrolytic gas under a pressure equal to its partial pressure in the diluted sample. C. F. B.

**Affinity Constants and Constitution of Organic Acids.** By BOHDAN SZYSZKOWSKI (*Zeit. physikal. Chem.*, 1897, **22**, 173—188).—The first series of acids investigated were chiefly derivatives of hydracrylic acid, the molecular conductivity and affinity constants being determined at 25°. In compounds containing secondary hydroxyl, the substitution of an alkyl group for hydrogen causes in general a decrease of the affinity constant, whilst the introduction of phenyl gives rise to a very marked increase. In acids containing tertiary hydroxyl, displacement of the hydrogen by hydrocarbon radicles always causes a slight increase, so that the effect of substitution by one and the same substituent is not dependent on its electrochemical character only. The constants of the secondary compounds are also throughout considerably less than those of the corresponding tertiary compounds. The affinity constants of unsaturated acids are considerably greater than those of the corresponding saturated acids, whilst the passage to the acetylenic compound is marked by a still further increase. As the constant also increases with approach of the electronegative groups, the author considers it probable that doubly-linked carbon atoms are nearer together than singly-linked atoms, whilst the triple linking indicates still greater proximity, the great instability of the latter compounds being due to this fact and the electrical repulsion of the atoms. The methyl group is also considered to be more electronegative

than hydrogen, and iso-radicles are more electronegative than those with normal structure. L. M. J.

**Velocity of the Reaction between Ferrous Chloride, Potassium Chlorate, and Hydrogen Chloride.** By ARTHUR A. NOYES and R. S. WASON (*Zeit. physikal. Chem.*, 1897, **22**, 210—221).—The reaction between ferrous sulphate and potassium chlorate in the presence of excess of sulphuric acid was found by Hood (Abstr., 1886, 301) to be of the second order, the velocity being proportional to the product of the concentrations of the two salts, the acid exerting an accelerative influence, the velocity increasing more rapidly than the acid concentration. The authors have studied the simpler case of the chlorides, and determined the velocity of reaction for several different sets of experiments, the velocity being calculated for both second order and third order reactions. Although with excess of acid the equation for a reaction of the second order apparently gives a satisfactory constant, yet the reaction is seen to be of the third order, this constant only varying irregularly from 157 to 184 through the whole set of experiments, whereas the second order constant increased regularly from 343 to 2130, whilst the acid concentration increased from n/10 to n/2. The actual course of the reaction, however, is not evident, as apparently more than three molecules of the compounds interact. The effect of temperature was investigated by means of a series of researches at 0°, 10°, 20°, 30°, 40°, and 50°, and the equation $\log K_1/K_2 = A(T_1 - T_2)/T_1T_2$ was found to give a constant value for $A$; this result accords with Van't Hoff's expression $d \log K/dt = A/T^2 + B$ when $B = 0$, which obtains in many other reactions (Abstr., 1889, 1044, 1103).

L. M. J.

**Velocity of Formation and Decomposition of Ethereal Salts.** By OSC. KNOBLAUCH (*Zeit. physikal. Chem.*, 1897, **22**, 268—276).—The reaction $C_2H_5{\cdot}OH + CH_3{\cdot}COOH \rightleftarrows CH_3{\cdot}COOC_2H_5 + H_2O$ was investigated in order to determine whether the velocity of decomposition of the ethereal salt obtained by a direct determination was actually equal to that deduced by calculation from the interaction of the alcohol and acid. By the 'direct' action, the ratio of the direct and inverse velocities was found to be 2·81, and from the 'inverse' action the ratio 2·67 was obtained, the mean value 2·74 being afterwards used in the calculations. By this means, the value $1{\cdot}01 \times 10^{-4}$ was obtained for the inverse (decomposition) velocity by calculation from the 'direct' reaction, and the value $0{\cdot}99 \times 10^{-4}$ was obtained from the measurement of the velocity of decomposition, the agreement being well within the experimental limits. L. M. J.

**Chemical Proportions.** By F. WALD (*Zeit. physikal. Chem.*, 1897, **22**, 253—267).—The author gives an account and explanation of the generally accepted laws of the atomic theory, and endeavours to prove that in compounds derived by the interaction of others the law of multiple proportions must hold, or as he finally states it: "If in a series of chemical compounds containing one common constituent we take such quantities that this constituent is present in equal quantity in all,

then the quantities of any other constituent which occur in different members of the series have a rational greatest common measure."

L. M. J.

## Inorganic Chemistry.

**A Convenient Method for Purifying Water.** By HARRY C. JONES and E. MACKAY (*Zeit. physikal. Chem.*, 1897, **22**, 237—238).—To obtain water suitable for physico-chemical measurements, the authors add some potassium permanganate and sulphuric acid to ordinary distilled water, and distil from a large flask. The vapour is passed into a retort sloping upwards, and containing distilled water, with potassium permanganate and sodium hydroxide; the end of the neck is packed with glass wool, and fitted with a receiver passing to a block tin condenser. No corks are employed, all packing being made with asbestos, and the glass wool is washed with hydrochloric acid, and heated in a stream of hydrogen. The first portion of the distillate is neglected, as it contains small quantities of ammonia, and large quantities can then be readily obtained with a conductivity of about $1\cdot5—2\cdot0 \times 10^{-6}$.

L. M. J.

**Fluoroxyiodates.** By RUDOLPH F. WEINLAND and O. LAUENSTEIN (*Ber.*, 1897, **30**, 866—869).—By the action of a 40 per cent. solution of hydrofluoric acid on iodates of the alkali metals and of ammonium, an oxygen atom is replaced by fluorine, the resulting difluoroxyiodates being well-defined crystalline substances. *Potassium difluoroxyiodate*, $KIO_2Fl_2$, forms large, colourless prisms, which in the dry condition are tolerably stable, but when exposed to moist air readily split up into the iodate and hydrofluoric acid. When heated, the difluoroxyiodate first melts and then decomposes, iodine and oxygen being evolved. Calcium chloride gives a precipitate of calcium fluoride, with a dilute aqueous solution of the salt.

*Ammonium difluoroxyiodate*, $NH_4IO_2Fl_2$, has the same crystalline form as the potassium salt, and behaves similarly to it, except when heated. *Sodium difluoroxyiodate* forms thin, hexagonal plates.

Contrary to the observation of Ditte, the authors find that iodic acid is without action on hydrofluoric acid, even when heated, the iodic acid being always recovered unchanged. Other fluoroxyiodates are being investigated.

J. F. T.

**Conditions of the Direct Combination of Hydrogen and Sulphur.** By H. PÉLABON (*Compt. rend.*, 1897, **124**, 686—688).—At 440°, the direct combination of hydrogen and sulphur is limited by the reverse reaction, and between 215° and 350° it is also limited, but not by the reverse reaction, since hydrogen sulphide is not decomposed by heat between these limits of temperature. Experiments have therefore been made with a view to ascertain the conditions of direct combination at temperatures below 440°. When hydrogen and sulphur are heated in sealed tubes which are opened after being allowed to cool,

the final composition of the gaseous mixture depends on the mass of sulphur employed, and the proportion of hydrogen sulphide is higher the higher the proportion of sulphur. The composition of the gaseous mixture in the cooled tube corresponds the more nearly with that of the gaseous mixture at the temperature of the experiment, the smaller the mass of the sulphur. When the proportion of the sulphur is low, but yet in excess, combination takes place more quickly the higher the temperature, and the maximum quantity of hydrogen sulphide that can be formed increases very regularly with the temperature. Experiments with larger masses of sulphur show that the quantity of hydrogen sulphide dissolved by the fused sulphur increases with the temperature. When the hydrogen is mixed with nitrogen, the maximum quantity of hydrogen sulphide formed is less than with pure hydrogen for the same time of heating, but, other conditions being the same, the difference is smaller the higher the temperature (compare this vol., ii, 207).

C. H. B.

**Sulphuryl Chloride.** By BRONISLAW PAWLEWSKI (*Ber.*, 1897, **30**, 765—767).—Owing to the literature of the subject being somewhat confused, the author considered it necessary to reinvestigate the properties of this compound. It boils (pressure = 760 mm.) at 69·1—69·2°, and has a sp. gr. = 1·66738, at 4°/20°; its refractive index $R_M = 35·92$, and its critical temperature after the first heating lies between 217—252°, depending on the quantity of liquid in the tube. The dissociation of the compound begins at 160°, and at 240—250° the vapour density is no longer normal.

J. F. T.

**The Freezing Point of Dilute Sulphuric Acid.** By WILHELM HILLMAYR (*Monatsh.*, 1897, **18**, 27—33).—The following results were obtained:

| | | | | | | |
|---|---|---|---|---|---|---|
| Percentage of sulphuric acid | 1·95 | 3·00 | 4·01 | 5·13 | 6·02 | 8·02. |
| Freezing point ... | – 0·78° | – 1·16° | – 1·65° | – 2·05° | – 2·55° | – 3·61°. |

These results agree well with those of Pfaundler and Schnegg (*Sitzungsber. Kaiserl. Akad. Wiss.*, 1875, **71**), and differ from those of Pictet (Abstr., 1895, ii, 106), who found values for the freezing point above 0°.

C. F. B.

**Sodium Thioselenide.** By CARL MESSINGER (*Ber.*, 1897, **30**, 805—806).—When selenium is boiled with aqueous sodium hydrosulphide in a current of hydrogen, it yields a solution from which alcohol precipitates *sodium thioselenide*, $Na_2SSe_2 + 5H_2O$, as a mass of dark red scales; the salt is hygroscopic and rapidly decomposes in the air, sodium sulphide and selenium being formed.

A. H.

**Nitrogen Sulphide.** By AMERICO ANDREOCCI (*Zeit. anorg. Chem.*, 1897, **14**, 246—250).—The author has commenced an examination of the chlorides of nitrogen sulphide with the object of elucidating the constitution of nitrogen sulphide. The nitrogen sulphide is prepared by the method described by Fordos Gélis (*Annalen*, 1851, **80**, 260), and melts at 178—179°. The determinations of the molecular weight by the boiling point method, using as solvents benzene and carbon

tetrachloride, agree with the formula $N_4S_4$, and confirm the determinations of Clever and Muthmann.

The yellow nitrogen sulphide chloride, $N_4S_4Cl_4$, is obtained by treating nitrogen sulphide suspended in carbon tetrachloride with chlorine. The chloride is stable when preserved under carbon tetrachloride, and crystallises without decomposition from hot, dry benzene. Determinations of the molecular weight by the cryoscopic method, using benzene as solvent, agree with the formula $N_4S_4Cl_4$. When the benzene solution is treated with water, it decomposes, and yields sulphurous anhydride and nitrogen chloride. When, however, it is treated directly with such a quantity of water that no appreciable rise in temperature takes place, it also yields an insoluble powder which contains nitrogen sulphide. When warmed, it yields the red chloride and other compounds; by the action of cold ammonia, it is reconverted into nitrogen sulphide, and is decomposed by absolute methylic and ethylic alcohols and phenol. When treated with dry hydrogen chloride in benzene solution, it yields a bright yellow compound which is only slowly decomposed by cold water, but immediately by lukewarm water.

E. C. R.

**Seleno-arsenates.** By CARL MESSINGER (*Ber.*, 1897, **30**, 797—805). —The author has prepared a number of salts intermediate between sodium arsenate, thioarsenate and selenarsenate by the action of the sodium compounds of sulphur, selenium, and oxygen on the selenosulphides of arsenic and in other similar ways. $Na_3AsO_2SSe + 10H_2O$ is prepared by the action of aqueous soda on arsenic triselenobisulphide, and crystallises in white, matted needles which decompose in the air. Acids cause the precipitation of sulphur and selenium from its solution. When arsenic diselenotrisulphide is dissolved in aqueous soda, the *salt* $Na_6As_2SeS_3O_4 + 20H_2O$ is produced in colourless, radiating needles which are tolerably stable in dry air. The mother liquor from this salt contains a *salt*, $Na_6As_2S_3Se_2O_3 + 20H_2O$, which crystallises in colourless needles. The *salt* $Na_6As_2S_7Se + 16H_2O$ is formed when arsenic diselenotrisulphide is treated with aqueous sodium hydrosulphide; the yellow prisms are stable in dry air, and acids precipitate arsenic trisulphide and sulphur from its solution. The *salt* $Na_3AsS_3Se + 8H_2O$ is produced when arsenic triselenodisulphide is treated with aqueous sodium hydrosulphide, and crystallises in well developed prisms; acids precipitate arsenic diselenotrisulphide from its solution. The *salt* $Na_3AsS_2Se_2 + 9H_2O$ is formed when arsenic triselenide (1 mol.) is fused with selenium (1 atom) and sulphur (1 atom) and the whole dissolved in sodium hydrosulphide; it crystallises in reddish-yellow prisms, and is decomposed in solution by dilute acids with evolution of hydrogen selenide and sulphide, whilst sulphur, selenium, and the triselenide and trisulphide of arsenic are deposited.

The *salt* $Na_3AsSSe_3 + 9H_2O$ is formed together with sodium monoselenothioarsenate when arsenic triselenide is dissolved in a mixture of sodium thioselenide and sulphide; it crystallises in red, hygroscopic prisms, and is decomposed by aqueous acids with evolution of hydrogen selenide and sulphide and precipitation of arsenic trisulphide and selenium. The *salt* $Na_9As_3S_2Se_2O_8 + 36H_2O$, obtained by dissolving arsenious oxide, sulphur, and selenium in aqueous soda, crystallises in

large, white prisms and is decomposed by aqueous acids with precipitation of sulphur and selenium, whilst a sulphoxy-salt remains in solution. The mother liquor from this salt contains the salt $Na_6As_2S_2SeO_5 + 24H_2O$, which closely resembles the foregoing. The *salt* $Na_6As_2S_5Se_3 + 16H_2O$ is obtained in brownish-yellow prisms by boiling sodium diselenothioarsenate, $Na_3AsS_2Se_2$, with sodium hydrosulphide, 2 molecules of the latter being necessary to replace a single atom of selenium by sulphur. It appears from a comparison of the solubilities of these salts that an arsenate is more soluble the greater the molecular weight of the acid residue contained in it. A. H.

**Conversion of Diamond into Graphite in a Crookes' Tube.** By HENRI MOISSAN (*Compt. rend.*, 1897, **124**, 653—655).—Diamonds which had been subjected to molecular bombardment in a Crookes' tube were completely blackened on the surface, and after prolonged treatment with nitric acid and potassium chlorate yielded graphitic oxide, which, when heated, changed into pyrographitic acid. The graphite was very slowly oxidised, and in this respect behaved like graphite formed at a high temperature. After four treatments with the oxidising mixture, the diamonds were still covered with a maroon-brown film of finely-divided carbon.

Since diamond is not converted into graphite in the oxyhydrogen blow-pipe, it is clear that the molecular bombardment must produce a temperature which exceeds 2000°. The behaviour of the graphite, in fact, indicates that it has been formed at a temperature similar to that of the electric arc, or about 3600°. C. H. B.

**Helium and Argon. III. Experiments which show the Inactivity of these Elements.** By WILLIAM RAMSAY and J. NORMAN COLLIE (*Proc. Roy. Soc.*, 1896, **60**, 53—56).—The paper contains a record of a number of experiments made to test the possibility of forming compounds of helium and argon.

On maintaining an electric arc, the electrodes of which were thin pencils of gas carbon, for several hours in an atmosphere of argon, a slow expansion took place, and on sparking the resulting gas with oxygen, carbonic anhydride was produced. It was at first thought that possibly a compound of argon had been formed, but on further examination it was shown that, although apparently all gas had been removed from the carbon electrodes before admitting argon, some carbonic anhydride still remained occluded and that prolonged heating had expelled this gas and converted it into the monoxide.

By the action of producer gas on a mixture of barium carbonate and carbon at the temperature of the electric arc, a substance rich in barium cyanide is obtained, from which all the nitrogen was recovered by Dumas' process. The whole of the nitrogen disappeared in presence of oxygen and soda, leaving no residue, thus showing that no argon had entered into combination.

A mixture of argon with the vapour of carbon tetrachloride was exposed to the silent electric discharge from a powerful induction coil. Here again, although a considerable amount of other chlorides of carbon was produced, argon did not enter into the reaction, but was recovered without loss of volume.

In experimenting with helium, the gas was circulated over the reagent at a bright red heat, and observations made of any alteration in volume or any marked change in the reagent employed. In no case was there any reason to suspect that helium had entered into combination.

The following is a list of substances tried:—sodium, silicon, beryllium, zinc, cadmium, boron, yttrium, thallium, titanium, thorium, tin, lead, phosphorus, arsenic, antimony, bismuth, sulphur, selenium, uranium, chlorine, cobalt, platinum, mixtures of soda-lime and potassium nitrate and soda-lime and sulphur, and benzene.

It is pointed out that any compound of helium capable of existence will probably be endothermic, and the two methods of producing such a compound, namely, exposure to a high temperature and the influence of the silent electric discharge, have been tried in vain. It is therefore to be concluded that helium and argon are incapable of forming compounds. A. W. C.

**Amount of Argon and Helium contained in the Gas from the Bath Springs.** By LORD RAYLEIGH (*Proc. Roy. Soc.*, 1896, **60**, 56—57).—The refractivity found for the residue from the gas of the Bath springs after removal of all gases known until recently, was found to be 0·896 referred to air. The proportional amount of helium is, therefore, 8 per cent., or 1·2 parts per thousand of the original volume. A. W. C.

**Drying and Deliquescence of Certain Salts.** By F. W. SMITHER (*Amer. Chem. J.*, 1897, **19**, 227. Compare Hake, *Proc.*, 1896, **12**, 33).—Tabulated records of the relative power possessed by certain inorganic salts of absorbing and retaining moisture are given. From these it would appear that lithium chloride, which is extremely hygroscopic at ordinary temperatures, is soon rendered anhydrous when heated in a steam bath at 97—98°. Calcium chloride, under similar conditions, retains less than $1H_2O$ after from 30—40 hours' heating, and afterwards loses and regains a small fraction of this amount repeatedly. Calcium nitrate behaves in much the same way. Both the chloride and nitrate of magnesium retain $1H_2O$ obstinately, and then lose water and acid gradually, some magnesium hydroxide being formed.

When the same salts are exposed to an atmosphere nearly saturated with moisture, they continue to absorb water most conspicuously, lithium chloride taking up more than 15 times its weight. During the exposure, a period is noticed when this salt ceases to absorb moisture, and the others lose in weight, but afterwards an increase in weight is noticed in all cases.

The author concludes that these salts do not form any hydrates when in the liquid state at ordinary temperature. A. W. C.

**Micrographic Study of some Italian Cements.** By LORENZO BUCCA and GIUSEPPE ODDO (*Gazzetta*, 1896, **26**, ii, 549—554).—The authors have examined three Italian cements, and criticise Le Chatelier's conclusions. (Compare Oddo and Manzella, Abstr., 1896, ii, 246.) W. J. P.

**Hydrates of Cadmium Sulphate.** By FRANZ MYLIUS and ROBERT FUNK (*Ber.*, 1897, **30**, 824—833).—The authors confirm Etard's

work (Abstr., 1888, 645) on the solubility of ordinary crystallised cadmium sulphate, $3CdSO_4 + 8H_2O$. The solubility reaches its maximum at 74°, when the percentage of substance dissolved is 46·7; from 74° to 100°, the solubility rapidly diminishes. When a saturated solution of cadmium sulphate is slowly evaporated at 70°, large crystals of the ordinary hydrate, $3CdSO_4 + 8H_2O$, are obtained, but if evaporated at 80°, a microcrystalline powder is deposited. The same powder is obtained at 100°; it consists of the hydrate $CdSO_4 + H_2O$, and does not lose its water of crystallisation at 100°. The sudden drop in the solubility of the ordinary hydrate at 74° is no doubt due to its conversion into the hydrate $CdSO_4 + H_2O$, which, at the ordinary temperature, slowly combines with water to form the ordinary hydrate.

A new hydrate, $CdSO_4 + 7H_2O$, is obtained when a solution of cadmium sulphate, saturated at 74°, is suddenly cooled to below −17°; on raising the temperature, the greater part of the mixture melts, but a small quantity of a granular precipitate remains behind; this needs to be carefully separated, and consists of the hydrate $CdSO_4 + 7H_2O$. The moist compound appears to be stable at temperatures below +4°; at this temperature, however, it is slowly converted into the ordinary hydrate. The solubility of the new hydrate increases slowly from 44·45 per cent. ($CdSO_4$) at −17° to 48·7 per cent. ($CdSO_4$) at −4·5°.

According to the authors, the ordinary hydrate does not effloresce on exposure to the air; they have, further, been unable to obtain the hydrate $2CdSO_4 + 5H_2O$ described by Rose (*Ann. Phys. Chem.*, **85**, 305), or the hydrate $CdSO_4 + 4H_2O$ described by Stromeyer. Ordinary crystallised cadmium sulphate readily effloresces, and, when powdered, loses all its water at 100°; this is due to small quantities of acid contained in the crystals; when quite free from acid, the crystals are extremely stable.

At 0°,

1 mol. $MgSO_4 + 7H_2O$ requires 18·9 mols. $H_2O$ for solution.
,, $ZnSO_4 + 7H_2O$ ,, 13·4 ,, ,, ,, ,,
,, $CdSO_4 + 7H_2O$ ,, 3·4 ,, ,, ,, ,,

That is, for this temperature the solubility increases with the atomic weight of the metal. J. J. S.

**Earth contained in Monazite Sands.** By PAUL SCHÜTZENBERGER and O. BOUDOUARD (*Compt. rend.*, 1897, **124**, 481—486).—The crystallised cerium sulphate prepared from monazite sands contains an oxide of higher molecular weight than that contained in cerium sulphate prepared from cerite.

After removal of didymium, lanthanum, and thorium, fractional crystallisation of the sulphate yields (1) a cerium with an atomic weight a little below 138, the solution of which is not precipitated by cupric oxide; (2) a cerium with an atomic weight of about 148, the sulphate of which is precipitated by cupric oxide, and also by sodium sulphate; (3) a cerium of atomic weight about 157, the sulphate of which is precipitated by cupric oxide, but not by sodium sulphate, and is characterised by a peculiar, gummy appearance which its aqueous solutions acquire during concentration. All three oxides yield yellow ceric salts which are converted on heating into white cerous salts, and they all behave in the same way with hydrogen peroxide in presence of

sodium hydroxide, and with ammonium oxalate. Their chlorides yield identical spark spectra.

A fraction soluble in normal ammonium oxalate solution and not precipitated by sodium sulphate does not give the cerium reactions but belongs to the thorium group. The sulphates of the metals allied to cerium, but of higher atomic weight, yield an intermediate oxide and not a dioxide when they are strongly heated, and this explains the differences observed between the analytical results obtained by precipitating the sulphuric acid with barium chloride on the one hand and by strongly heating the sulphate on the other (compare Abstr., 1896, ii, 475). C. H. B.

**The Earths in Monazite Sands.** By G. URBAIN and E. BUDISCHOVSKY (*Compt. rend.*, 1897, **124**, 618—621).—The authors have endeavoured to ascertain whether the earths from monazite sands contain a constituent with an atomic weight of about 100. The sands were those examined by Schützenberger and Boudouard, and the experiments were made with the fraction precipitable by sodium thiosulphate. The oxides were converted into nitrates, and afterwards into acetonylacetonates by precipitating with ammonia and adding acetylacetone. The acetylacetonates were fractionated by crystallisation from alcohol and from benzene. The fraction with atomic weight 95—97 gave by this method as extreme values 96 and 97. The fraction 98—102 gave extreme values 98 and 108, and the fraction 103—105 gave extreme values 97 and 112. It is noteworthy that the lowest numbers are considerably higher than the atomic weight of yttrium, and that the atomic weight of the mother liquor was in all cases higher than that of the crystals.

In determining the atomic weights, the nitrates were converted into sulphates and the latter were heated first in sulphur vapour and then at gradually increasing temperatures until the weight was constant, and finally the sulphates were converted into oxides by heating in a double platinum crucible (compare Schützenberger and Boudouard, preceding abstract). C. H. B.

**Occurrence of Gallium in the Clay-ironstone of the Cleveland District of Yorkshire: Determination of Gallium in Blast-furnace Iron from Middlesbrough.** By W. NOEL HARTLEY and HUGH RAMAGE (*Proc. Roy. Soc.*, 1897, **60**, 393—407).—The blast furnace iron from Middlesbrough is found to contain 1 part of gallium in 33,000 parts of crude iron, which is more than in the richest source of this element hitherto known. The element is contained in the crude ore, and becomes concentrated in the metal.

The method employed in this examination was that of fractional precipitation by means of zinc, and also by ammonium acetate, with spectrographic analysis of the precipitates, supplemented by gravimetric determinations of the purified gallium sesquioxide.

A specimen of manganese ore examined was found to contain both gallium and indium, which is remarkable, as hitherto the latter has been found only in zinc blendes.

Clay ironstones from Middlesbrough, Whitby, Northamptonshire, and St. Andrews were all found to contain gallium. A. W. C.

**Action of Iron on Solutions of Metallic Nitrates.** By JEAN B. SENDERENS (*Bull. Soc. Chim.*, 1897, [iii], **15**, 691—700. Compare Abstr., 1897, ii, 171).—The author has studied the action of different kinds of iron (wrought iron piano wire, &c.) on dilute solutions of silver salts, and finds that unworked iron is far more active than worked iron, precipitating the silver readily from dilute solutions of the nitrate. This he attributes to a difference in the physical condition in the different samples of iron. M. W. T.

**Ferric Alkali Salts of Sulphurous Acid.** By KARL A. HOFMANN (*Zeit. anorg. Chem.*, 1897, **14**, 282—292).—The *salt* $Fe_2(SO_3)_4SO_4K_4 + 5H_2O$ is obtained by treating potassium iron heptanitrososulphonate, $KS_3Fe_4(NO)_7$, dissolved in alcohol with a solution of sodium hydrogen sulphite, and allowing the mixture to remain at the ordinary temperature for about 14 days. It forms a yellow, lustrous mass of microscopic needles, is insoluble in cold water, and when boiled with water is decomposed into ferric hydroxide and a soluble, ferrous salt. It dissolves immediately in 20 per cent. hydrochloric acid, and the solution gives a blue precipitate with potassium ferrocyanide, and only a brown coloration with potassium ferricyanide, whence the author concludes that the compound is a ferric salt. On boiling the hydrochloric acid solution, partial reduction of the ferric salt takes place.

The *salt* $Fe(SO_3)_2SO_4K_3$ is obtained by digesting the heptanitrososulphonate for about 1 month with sodium hydrogen sulphite at 4°. It crystallises in beautiful, lustrous, dark yellow leaflets, is almost insoluble in cold water, and behaves like the preceding salt when boiled with water or dilute acid.

The *salt* $FeSO_3SO_4K$, obtained by treating finely powdered iron ammonium alum with potassium hydrogen sulphite, crystallises in slender, double refracting needles. It is but sparingly soluble in cold water, and the solution contains ferric salt only. When heated for some time with water at 80—90°, ferrous sulphate and potassium sulphate are dissolved, and a yellow residue is obtained which is soluble with difficulty in dilute acids with evolution of sulphurous anhydride. It dissolves readily in cold, dilute hydrochloric acid, and the bright yellow solution gives a blue precipitate with potassium ferrocyanide, and only after boiling a blue with potassium ferricyanide.

The *salt* $FeSO_3SO_4NH_4 + H_2O$, obtained by treating ammonium alum with ammonium or sodium hydrogen sulphite, crystallises in slender, yellow needles, is only very slightly soluble in cold and hot water, and by prolonged boiling with water is converted into a red powder, with evolution of sulphurous anhydride. It is easily soluble in cold, dilute hydrochloric acid with evolution of sulphurous anhydride. When treated with ammonia or dilute alkali, it is decomposed, with formation of a brown, flocculent precipitate.

The *salt* $Fe(SO_3)_2SO_4Na_3 + 6H_2O$, is obtained by digesting sodium iron heptanitrososulphonate with sodium hydrogen sulphite for some days. It crystallises in lustrous, flat, yellow prisms, and is very similar to the corresponding potassium salt.

The *salt* $Fe_2SO_4(SO_3)_4H_2Na_2 + 2H_2O$ is obtained by dissolving freshly prepared ferric hydroxide in a concentrated solution of sodium hydrogen

sulphite and sulphurous acid. On evaporating the solution over sulphuric acid, a red, amorphous substance separates at first; but after this has been removed, a crystalline mixture of the salt together with the preceding salt is obtained. It can be separated by treating the mixed crystals with a solution of sodium hydrogen sulphite, and crystallises in bright olive-green needles. E. C. R.

**Metallic Ammonium Compounds. II.** By KARL A. HOFMANN (*Zeit. anorg. Chem.*, 1897, **14**, 263—281).—The reactions of the triammine salt, $C_2S_7Co_2(NH_3)_6$, already described (*Zeit. anorg. Chem.*, **11**, 379) have been examined to ascertain if more than 3 mols. of ammonia to 1 mol. of cobalt can be retained in the compounds.

The *compound* $C_2S_8Co_2(NH_3)_6O_3$ is obtained together with the salt, $CoS_2O_6(NH_3)_5$, when the above triammine salt is allowed to remain some months under 10 per cent. aqueous ammonia. The two compounds are separated by washing out the first salt, which crystallises in thin plates, with strong ammonia. The salt $CoS_2O_6(NH_3)_5$ is sparingly soluble in cold water, more easily in hot water, and when boiled suddenly deposits a bright brown precipitate. It dissolves to a reddish-yellow solution in warm soda solution, and on boiling deposits a dark brown precipitate. With dilute hydrochloric acid and barium chloride, it yields barium sulphate, cobaltous chloride, and sulphurous acid. The compound is, therefore, a cobaltisulphite ammonia salt. This is also proved by the formation of the salt $C_2S_7Co_2(NH_3)_6$ by boiling the ammonium cobaltous salt of cobaltisulphurous acid with ammonia.

The ammonia molecules of the salt $C_2S_7Co_2(NH_3)_6$ are only removed with difficulty by acids. Fuming hydrochloric acid at the ordinary temperature yields a compound of the formula $Co_2C_2ClS_{14}O_{10}H_{26}$ as a black, crystalline precipitate, and a blue solution is left. Acetic acid (60 per cent.), after many days at the ordinary temperature, yields the *compound* $(CS_3)_3Co_2S(NH_3)_2,C_2H_4O_2 + 4H_2O$, whereby hydrogen sulphide is liberated and much cobalt dissolved. This salt crystallises in small, lustrous, black scales. Acetic anhydride acts very slowly, and after 4 days a *compound*, $C_2S_8Co_25NH_3$, was obtained as a black, lustrous, crystalline powder.

The *compound* $C_2S_8Co_2(NH_3)_5H_2O$ is obtained by the action of diazobenzene nitrate on the triammine salt at 0° after 24 hours. It forms black, prismatic crystals, is slightly soluble in water, and gives an intense green coloration with dilute sodium hydroxide. With a large mass of diazobenzene nitrate and more prolonged action, more ammonia is eliminated, but the author was unable to isolate the compound formed.

Erdmann's cobalt triammine nitrite, $Co(NO_2)_3(NH_3)_3$, is obtained by treating the triammine salt suspended in water with nitrous oxide. Sulphur and carbon bisulphide are separated during the reaction. It crystallises from water in brownish-yellow needles.

The above results show that no ammonia is combined between the cobalt and sulphur, for, if this were the case, groups of the constitution $CoNH_3 \cdot S \cdot NH_3Co$ or $Co \cdot NH_3 \cdot S \cdot C$ would be formed, and the compound $C_2S_7Co_2(NH_3)_6$ should give the reactions of hydrogen sulphide or thiocarbonic acid.

The compound $C_2S_7Co_2(NH_3)_5 + 2H_2O$ is obtained by treating cobaltic hydroxide with 10 per cent. ammonia and carbon bisulphide and allowing the mixture to remain for some time below 10°. It crystallises in long, brownish-red needles, and decomposes gradually at the ordinary temperature with evolution of hydrogen sulphide.

The *compound* $CS_4CoH,3NH_3$ which is obtained by allowing the mixture employed for the preparation of the preceding compound to remain at the ordinary temperature for 4—5 days, crystallises in black prisms resembling hornblende, and is the compound from which the triammine salt, $C_2S_7Co_2(NH_3)_6$, is formed by the elimination of hydrogen sulphide. It dissolves in water with an intense yellow coloration, and in sodium hydroxide or ammonia to a greenish-yellow solution; neither of these solutions gives a coloration with sodium nitroferrocyanide, or a deposit of silver sulphide on a piece of metallic silver. It, therefore, does not contain ammonia between the cobalt and sulphur.

*Cupric trithiocarbonate ammonia*, $CS_3CuNH_3$, is obtained by treating a mixture of cuprous chloride and excess of ammonia (10 per cent.) with carbon bisulphide at 0°; after remaining 3 days, a separation of hair-like crystals takes place, and after another 2 days these are converted into the new salt. This crystallises in thick, green tablets having a metallic lustre, is only very sparingly soluble in strong ammonia, and gives a brown solution and a precipitate of brownish-black flocks with dilute sodium hydroxide. It is also obtained by the action of ammonia and carbon bisulphide on copper sulphate at 10°. When allowed to remain with 60 per cent. acetic acid for 4 days, it yields the *compound* $CS_3Cu_2S$, which crystallises in lustrous, bronze-coloured crystals.

The *compound* $C_2S_5Cu_3(NH_3)_6O_6$ is obtained by allowing a mixture of copper sulphate, 6 per cent. ammonia, and carbon bisulphide to remain at 0° for 4—5 weeks. It crystallises in black, monosymmetric tablets, dissolves easily in ammonia with a blue coloration, is insoluble in water, and is not decomposed when allowed to remain over sulphuric acid. Dilute sodium hydroxide has only a surface action on the compound; but it is completely decomposed by concentrated sodium hydroxide with formation of cupric hydroxide and sulphuric acid.

*Zinc trithiocarbonate ammonia*, $CS_3Zn(NH_3)_2$, is obtained by dissolving zinc sulphate in 10 per cent. ammonia, then adding excess of ammonia and after cooling at 5°, shaking the mixture with carbon bisulphide; it is a bright, salmon-coloured, crystalline powder. Cadmium sulphate forms a similar compound, which crystallises in lustrous, colourless plates, but decomposes with formation of cadmium sulphide when dried.

The thiocarbonates of platinum, iridium, and rhodium combine very easily with ammonia. The *salt* $Pt(NH_3)_2S_3C + H_2O$ is obtained from potassium platinous chloride, strong ammonia, and carbon bisulphide. It crystallises in long, red needles, is insoluble in cold water, ammonia, or sodium hydroxide, and gives up its water of crystallisation when allowed to remain in a vacuum over sulphuric acid. It gives no coloration with sodium nitroferrocyanide, nor a mercaptan nor methyl sulphide when boiled with methylic iodide. Under certain conditions,

which have not yet been determined, the *salt* $Pt_2Cl_2(NH_3)_4S_3C$ is formed, and crystallises in slender, red needles. The *salt* $C_2S_5PtNH_3$ is obtained from ammonium platinum chloride, ammonia, and carbon bisulphide; it crystallises in lustrous, black crystals, and is easily soluble in dilute sodium hydroxide. E. C. R.

**Double Chromates.** By JOSEF ZEHENTER (*Monatsh.*, 1897, **18**, 48—55).—If a solution of potassium dichromate (1 mol.) is treated with sodium carbonate (1 mol.), concentrated by heating, and finally allowed to crystallise in a vacuum over sulphuric acid, the following salts crystallise out in succession (the solubilities given represent the parts dissolved by 100 parts of water at 14°; the specific gravities were determined at 15°):—$3K_2CrO_4,Na_2CrO_4$, sp. gr. 2·719, solubility 64·2; $3K_2CrO_4,Na_2CrO_4 + \frac{1}{2}H_2O$, sp. gr. 2·575, solubility 66·4;

$Na_2CrO_4 + 4H_2O$;

the yields of these corresponded to 40, 30, and 20 per cent. respectively of the chromate taken.

By treating a solution of ammonium dichromate with potassium carbonate in molecular proportion, and precipitating with alcohol, the salt $3K_2CrO_4,2(NH_4)_2CrO_4$ is obtained; sp. gr. 2·403. By using sodium, instead of potassium, carbonate, the salt $NaNH_4CrO_4 + 2H_2O$ is obtained; sp. gr. 1·842. These two salts are decomposed by water or by heating.

From potassium dichromate and lithium carbonate, mixed in aqueous solution, the salt $K_2CrO_4,Li_2CrO_4 + \frac{1}{2}H_2O$, is obtained by evaporation in a vacuum; sp. gr. 2·539. C. F. B.

**Stannic Chlorobromides.** By J. ADOLPHE BESSON (*Compt. rend.*, 1897, **124**, 683—685).—The isolation of the stannic chlorobromides is difficult because they very readily decompose when distilled, even in a vacuum. They are produced by the action of dry hydrogen bromide on stannic chloride at 0°, or by the action of bromine on stannous chloride in presence of carbon tetrachloride, in which the products are soluble but the stannous chloride is not. The products are much more easily separated and obtained in a pure condition when prepared by the second method; the crude product is twice rapidly fractionated under very low pressure, and the fractions are further purified by fractional crystallisation at low temperatures.

Stannic chlorobromides are colourless liquids, which fume in moist air, with formation of crystalline hydrates, and dissolve in, and are decomposed by, water. They rapidly decompose into stannic chloride and stannic bromide when heated. The chlorobromide, $SnCl_3Br$, boils at about 50° under a pressure of 30 mm., and about 45° under a pressure of 20 mm., and melts at about −31°; sp. gr. = 2·51 at 13°. The chlorobromide, $SnCl_2Br_2$, boils at about 65° under a pressure of 30 mm., and melts at −20°; sp. gr. = 2·82 at 13°. The chlorobromide, $SnClBr_3$, boils at about 73° under a pressure of 30 mm., and melts at 1°; sp. gr. = 3·12 at 13°. C. H. B.

**Action of Heat on Antimony Tetroxide.** By HENRI BAUBIGNY (*Compt. rend.*, 1897, **124**, 560—562).—Antimony tetroxide, although stable at 800°, is decomposed at the melting point of silver, with forma-

tion of the trioxide. At the melting point of gold, the decomposition of the tetroxide and volatilisation of the trioxide are very rapid.

C. H. B.

**Liquation of certain Alloys of Gold.** By EDWARD MATTHEY (*Proc. Roy. Soc.*, 1896, **60**, 21—35).—On account of certain processes now employed for extracting gold from its ores, there has been introduced into this country a series of new alloys of gold and the base metals, principally lead and zinc, whose presence renders it impossible to estimate the true value of gold ingots by assaying in the ordinary way.

The author has found that samples taken from the opposite ends of the same ingot gave, on assaying, a fineness for gold varying between 439·35 and 662·45; and, in a second example, samples from the same end of an ingot varied between 332·5 and 652·0. In such cases, in order to obtain the true fineness, it becomes necessary to separate the gold in mass.

Numerous experiments were made to ascertain what effect the abovementioned base metals exert when mixed with gold. When alloyed with lead alone, the gold seems to liquate towards the centre of the mass; with 25 per cent. of lead and zinc, the same phenomenon occurs, but here the result is complicated, as gravity sends the gold to the lower portion of the mass. If, however, silver is added in considerable quantity as well as lead and zinc, the alloy has a constant composition.

The cooling curves of these alloys also indicate that the presence of silver has a decided effect, as it acts as a solvent for both lead and zinc. The curve for an alloy of gold, copper, zinc, and lead shows that the mass solidifies as a whole at 635°, with decided breaks at 407° and 247°, temperatures which are evidently connected with the solidifying points of lead and zinc. If 10 per cent. of silver be added to the above alloy, only a slight break is noticed at 206°, and, on assaying, the mass is proved to have a fairly uniform composition. Provided not more than 30 per cent. of the base metals be present, silver will dissolve them with the above result. A. W. C.

**Action of Phosphorus on Gold.** By A. GRANGER (*Compt. rend.*, 1897, **124**, 498—499).—Phosphorus can be distilled off finely divided gold without affecting it, but at about 400° its vapour attacks the metal, which swells up and becomes grey. At a dull red heat, the gold is not attacked by the phosphorus vapour, and hence the combination only takes place between narrow limits of temperature. If the tube is suddenly cooled whilst full of phosphorus vapour, a definite phosphide, $Au_3P_4$, is obtained; this is a very friable, grey compound, which is decomposed when heated in air, and is also slowly but completely decomposed when heated in a current of carbonic anhydride at the temperature at which it was formed; it is attacked by chlorine and aqua regia. Since phosphorus has no action on gold at high temperatures, a thin film of the metal forms a valuable protection to porcelain tubes, dishes, &c., which are exposed to phosphorus vapour at high temperatures. C. H. B.

**Mixed Platinohaloids.** By ARTURO MIOLATI (*Zeit. anorg. Chem.*, 1897, **14**, 237—245).—The compound $K_2PtCl_4Br_2$, obtained by L.

Pitkin by adding potassium bromide to an aqueous solution of hydrogen platinochloride, is also obtained by treating potassium platinosochloride, $K_2PtCl_4$, with bromine, whereby a reaction takes place which is quite analogous to the addition of bromine or chlorine to the potassium platinonitrite or platinocyanide. The crude product, which on analysis gives numbers very nearly agreeing with those required by theory, can be recrystallised from warm water, and forms beautiful, orange-red, dichroic cubes; from the mother liquors, however, a less pure crystallisation is obtained. The analyses of several fractional separations show that the compound is very gradually decomposed. Determinations of the electric conductivity show that the decomposition in dilute, cold, aqueous solution is very gradual and approaches a maximum. The first determination observed at once after the complete solution of the salt is normal.

The salt $K_2PtCl_6$, as regards its electric conductivity, behaves as the potassium salt of the acid $H_2PtCl_6$. The corresponding bromine compound, $K_2PtBr_6$, on the other hand, behaves in a manner analogous to the salt $K_2PtCl_4Br_2$. A mixture of the two salts, $K_2PtCl_6$ and $K_2PtBr_6$, in the proportion corresponding with the salt $K_2PtCl_4Br_2$, gave numbers differing from those obtained for the salt $K_2PtCl_4Br_2$, but the differences were not sufficient to determine if the same or a different system is contained in the solutions. E. C. R.

---

## Mineralogical Chemistry.

**Mineral Tallow from Danby, Vermont.** By L. E. Smoot (*Amer. Chem. J.*, 1897, **19**, 233).—The substance is of a soft, smooth putty-like consistence, is nearly white, and on drying hardens to a pith-like mass. It is non-crystalline, and when heated in a closed tube, chars, giving off a small amount of alkaline vapours. Analysis gave:

| | CaO. | MgO. | $CO_2$. | $SiO_2$. | $H_2O$ lost in desiccator. | $H_2O$ at 130°C. | Organic matter by difference. | N. | Total. |
|---|---|---|---|---|---|---|---|---|---|
| | 7·63 | 0·04 | 6·04 | 0·52 | 84·37 | 1·01 | 0·39 | — | 100·00 |
| Dried | 52·19 | 0·27 | 41·31 | 3·57 | — | — | 2·66 | (0·053) | 100·00 |

A. W. C.

**Periclase from Långban.** By S. A. Hjalmar Sjögren (*Jahrb. f. Min.*, 1897, i, 11; from *Geol. Fören. i Stockholm Förh.*, 1895, **17**, 288—291).—Grains of periclase, which are surrounded by a shell of brucite, occur with hausmannite in a limestone poor in magnesium at Långban, Sweden. The green colour of the periclase is due to numerous enclosures arranged in zones parallel to the octahedral faces; these enclosures are mostly octahedral in form, but are sometimes elongated, and have their axes coinciding in direction with the axes of the periclase. As shown by the high content of manganous oxide, 8—9 per cent. in the periclase, these enclosures must be manganosite. In

the brucite shell, this manganosite is represented as brown and black hydrated oxides of manganese. The periclase is an original constituent of the limestone. L. J. S.

**Analysis of Dolomitic Marble from Texas, Md.** By GEORGE G. BUCK (*Amer. Chem. J.*, 1897, **19**, 234).—The marble has a faint yellow tint, with a sp. gr. = 2·865, and hardness 3·5°. Its composition is :

| CaO. | MgO. | FeO. | $CO_2$. | $SiO_2$. | Total. |
|---|---|---|---|---|---|
| 31·58 | 19·64 | 0·14 | 47·55 | 1·27 | 100·18 |

which approximates fairly to that of a true dolomite. A. W. C.

**Composition of Turquoise.** By ADOLPHE CARNOT (*Bull. soc. fran. min.*, 1895, **18**, 119—123. Compare Abstr., 1894, ii, 355).—Turquoise with microcrystalline structure from a pegmatite at Burrow Mountains, Grant Co., New Mexico, gave the following results on analysis :

| $P_2O_5$. | $Al_2O_3$. | CuO. | FeO. | CaO. | $H_2O$. | Quartz and clay. | Total. |
|---|---|---|---|---|---|---|---|
| 28·29 | 34·32 | 7·41 | 0·91 | 7·93 | 18·24 | 2·73 | 99·83 |

Also traces of MnO, MgO, and fluorine. This agrees fairly closely with the formula previously given, namely, $P_2O_5(Al_2,Fe_3Ca_3Cu_3)O_3 + Al_2O_3 + 5H_2O$. L. J. S.

**Copiapite and Botryogen from Falun.** By S. A. HJALMAR SJÖGREN (*Jahrb. f. Min.*, 1897, i, 29 ; from *Geol. Fören. i Stockholm Förh.*, 1895, **17**, 306—312).—Copiapite occurs on botryogen at Falun, Sweden, as a fine-crystalline aggregate of sulphur, to citron-yellow colour. The minute, monosymmetric crystals are tabular parallel to (010) and have a rhombic outline ; the optic axial plane is approximately parallel to (409) (not ($\bar{4}$09) as given by Linck), with the obtuse negative bisectrix perpendicular to (010). Analysis by Mauzelius gave the results under I ; sp. gr. 2·08. Calculating FeO, MnO and ZnO with the MgO, this gives the formula $Fe_2(SO_4)_3 + 2Fe(OH)SO_4 + MgSO_4 + 21H_2O$. Taking this with other analyses, the author gives $20H_2O$ as being the most probable, but considers that it might vary slightly.

| | $SO_3$. | $Fe_2O_3$. | FeO. | MnO. | ZnO. | MgO. | $H_2O$. | Insol. | Total. |
|---|---|---|---|---|---|---|---|---|---|
| I. | 38·48 | 24·46 | 0·27 | 0·16 | 0·58 | 3·75 | 32·39 | 0·09 | 100·18 |
| II. | 37·78 | 19·60 | 0·38 | 0·44 | 2·50 | 7·31 | 31·39 | 0·21 | 99·61 |

The botryogen gave analysis II, by Mauzelius ; sp. gr. 2·13 ; this agrees with an old analysis of Cleve's of the Falun mineral, and leads to the formula $MgFe'''(OH)(SO_4)_2 + 7H_2O$. L. J. S.

**Tilasite or Fluor-adelite from Långban.** By S. A. HJALMAR SJÖGREN (*Jahrb. f. Min.*, 1897, i, 25—26 ; from *Geol. Fören. i Stockholm Förh.*, 1895, **17**, 291—294).—Irregular grains of this new mineral are found with hausmannite, berzeliite and calcite in a grey limestone at Långban, Sweden. It is grey to pale violet in colour ; the lustre on the fractured surfaces is greasy, and on the cleavage surfaces vitreous. Analysis by Mauzelius gave :

| $As_2O_5$. | FeO. | MnO. | CaO. | MgO. | $Na_2O$. | $H_2O$. | Cl. | F. | Total less O for F. |
|---|---|---|---|---|---|---|---|---|---|
| 50·91 | 0·14 | 0·16 | 25·32 | 18·22 | 0·29 | 0·28 | 0·02 | 8·24 | 100·11 |

The formula, $2CaO,MgO,MgF_2,As_2O_5$, is like that of adelite (Abstr., 1893, ii, 420), but with fluorine in place of OH. The optical examination of cleavage flakes shows the mineral to be anorthic.

L. J. S.

**Mauzeliite, a New Antimonate from Jakobsberg, Sweden.** By S. A. Hjalmar Sjögren (*Jahrb. f. Min.*, 1897, i, 26—27; from *Geol. Fören. i Stockholm Förh.*, 1895, 17, 313—318).—Mauzeliite occurs, with a rose-red mineral which is probably svabite, in a calcite vein in a mixture of hausmannite, calcite, garnet, schefferite and manganophyllite at Jakobsberg, Sweden. The isometric crystals are 5—10 mm. across, of a brown colour, and show the forms {111}, {100}, {311}. Hardness 6—6·5; sp. gr. 5·11. Owing to cloudy enclosures, it is difficult to obtain pure material for analysis; the mean of the two analyses by Mauzelius is:

| $Sb_2O_5$. | $TiO_2$. | PbO. | FeO. | MnO. | CaO. | MgO. | $K_2O$. | $Na_2O$. | $H_2O$. | F. |
|---|---|---|---|---|---|---|---|---|---|---|
| 59·25 | 7·93 | 6·79 | 0·79 | 1·27 | 17·97 | 0·11 | 0·22 | 2·70 | 0·87 | [3·63] |

The fluorine could not be determined, and is given above as the difference; neglecting it, the formula is given as $Ti(SbO_4R^{II})_4 = 4R^{II}O,2Sb_2O_5,TiO_2$. The mineral is related to monimolite and atopite [and more closely to lewisite, Abstr., 1895, ii, 508].

L. J. S.

**Analyses and Constitution of Vesuvian [Idocrase].** By S. A. Hjalmar Sjögren (*Jahrb. f. Min.*, 1897, i, 21—23; from *Geol. Fören. i Stockholm Förh.*, 1895, 17, 267—278).—Under I is given the mean of two partial analyses by Mauzelius of pure, transparent manganidocrase from the Harstig mine, Pajsberg, Sweden; loss on ignition, 2·06 per cent.; a trace of copper or nickel is present; sp. gr. 3·45—3·433. II is the mean of three partial analyses by Mauzelius of green idocrase from Vaticha, near Nijni Tagilsk, in the Urals; traces of chromium and phosphoric acid are present.

| | $SiO_2$. | $TiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MnO. | CaO. | MgO. | $K_2O$. | $Na_2O$. | $H_2O$. | F. | Total less O for F. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I. | 35·38 | — | 10·19 | 8·14 | — | 4·81 | 34·18 | 4·39 | 0·47 | 0·46 | 1·46 | 1·99 | 100·64 |
| II. | 36·82 | 0·40 | 15·14 | 4·29 | 0·37 | — | 36·22 | 3·72 | 0·12 | 0·18 | 3·13 | 0·46 | 100·66 |

The mean of a series of the newer analyses of idocrase gives the ratio $R^{IV}O_2 : R^{III}{}_2O_3 : R^{II}O : (H_2O,F_2) = 6:1·72:7·30:0·98$. Taking 0·72 $R^{III}{}_2O_3$ and 0·72 $(H_2O,F_2)$ to form the bivalent group $R^{III}(OH,F)$, and placing the remaining 0·26 $(H_2O,F_2)$ with $R^{II}$, this ratio becomes $RO_2 : R_2O_3 : RO = 6:1:9$. This gives the formula $[Al(SiO_4)_3R^{II}{}_4]_2R^{II}$, in which $R^{II} = AlOH,AlF,FeOH, Ca \ldots H_2$; in the simplest case, it becomes $Al_2(SiO_4)_6Ca_9$. This formula is discussed in relation to the fusion and alteration products, and the mode of occurrence of idocrase (compare Abstr., 1895, ii, 511).

L. J. S.

**Alteration of Chondrodite, Tremolite and Dolomite into Serpentine at the Ko mine, Nordmark.** By S. A. Hjalmar Sjögren (*Jahrb. f. Min.*, 1897, i, 19—21; from *Geol. Fören. i Stockholm Förh.*, 1895, 17, 294—306).—The mineral occurrences at the Nordmark mines in Sweden, and particularly the Ko mine, are very similar to those at the Tilly Foster iron mine, New York, there being a similarity in the alteration products, as well as with the fresh minerals. The

chondrodite which occurs in the dolomite is more often altered to serpentine than that which occurs in the iron ore; with this alteration, the honey-yellow colour becomes greyish-yellow, and the lustre changes from vitreous to waxy, but the edges of the crystals remain sharp. The crystals are often surrounded by a detachable shell of altered material. Analysis I was made by Anderson on material which in thin sections showed, besides homogeneous serpentine material, an opaque substance considered to be a very fine mixture of calcite and serpentine. Analysis II, by Mauzelius, is of more altered, and nearly homogeneous, material; at 115—120°, it lost 3·2 per cent. Deducting $CO_2$ and the corresponding amount of CaO to form $CaCO_3$, only II approaches to serpentine in composition. Constitutional formulæ, illustrating the processes of alteration, are given:

| | $SiO_2$. | $CO_2$. | $Fe_2O_3$. | FeO. | MnO. | CaO. | MgO. | $H_2O$. | F. | Total less O for F. |
|---|---|---|---|---|---|---|---|---|---|---|
| I. | 31·19 | 7·08 | — | 2·37 | 0·74 | 15·98 | 29·60 | 9·46 | 4·33 | 98·72 |
| II. | 42·07 | trace | 1·26 | 4·31 | 3·36 | 0·76 | 34·57 | 12·89 | 0·91 | 99·75 |
| III. | 24·83 | 18·07 | — | 1·53 | 0·72 | 23·44 | 23·93 | 6·65 | 1·95 | 100·30 |
| IV. | 42·30 | — | 1·50 | 1·66 | 1·51 | 0·22 | 37·75 | 14·14 | 1·15 | 99·75 |

Tremolite is frequently altered into serpentine; the crystal form remains, but the transparency and vitreous lustre are lost. The altered part is sharply separated from the unaltered, and usually consists of pure, fibrous serpentine. Analysis by Mauzelius gave III; at 120°, there is a loss of 2·16 per cent. After deducting $CaCO_3$, the remainder has the composition of serpentine.

Dolomite is also often altered into serpentine, and this frequently forms the matrix of the altered chondrodite and tremolite. It is greyish-green, has a greasy lustre, and a conchoidal to splintery fracture; in thin sections, it is seen to be structureless. Analysis by Mauzelius gave IV; at 120°, there is a loss of 4·5 per cent.; this corresponds with 2 mols. of serpentine + 1 mol. cerolite.

Chondrodite is sometimes altered to dolomite (or calcite). In these alterations, there has then been both serpentinisation and carbonatisation, and fluorine seems to have played a part. L. J. S.

**Physical-chemical Investigation of Desmine [Stilbite].** By Friedrich Rinne (*Jahrb. f. Min.*, 1897, i, 41—60).—When stilbite ($CaAl_2Si_6O_{16} + 6H_2O$) is placed in concentrated sulphuric acid, the loss of water is accompanied by a progressive change in the optical characters of the crystals; the optic axes vary their positions, passing through uniaxial positions four times. The same change takes place when the crystals are heated, and from the powdered mineral the following percentages of water are lost:

| 125° | 150° | 185° | 240° | 260° | 275° | 300° | 325° | 350° | 375° | 400° | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 4·27 | 8·09 | 10·32 | 12·10 | 13·21 | 13·86 | 14·69 | 15·28 | 15·49 | 16·05 | 16·53 | p.ct. |

Over sulphuric acid, and at 100° (1·5 per cent.) small amounts of hygroscopic water are lost; on ignition, there is a loss of 18·40 per cent. These changes are gradual, but the following stages can be distinguished:

| Temperature. | $CaAl_2Si_6O_{16}$ + | Uniaxial on | System. |
|---|---|---|---|
| 125° | $5H_2O$ | $(\bar{2}01)$ | Monosymmetric. |
| 150 | $4H_2O$ | (010) | ,, |
| 185 | $3H_2O$ | (001) | ,, |
| 250 | $2H_2O$ | $(\bar{2}01)$ | Passage to orthorhombic. |
| 350 | $H_2O$ | — | Orthorhombic. |
| Ignition | — | — | Amorphous. |

The name *metadesmine* is given to these dehydrated forms. These changes are analogous to those which take place in heulandite. By the action of dilute acids, birefringent forms of silica are produced as in heulandite (Abstr., 1896, ii, 368). L. J. S.

**Analyses and Constitution of Axinite.** By S. A. Hjalmar Sjögren (*Jahrb. f. Min.*, 1897, i, 23—24; from *Geol. Fören. i Stockholm Förh.*, 1895, **17**, 279—288).—The following analyses are given. I, Brown axinite from Nordmark; sp. gr. 3·3. II, ditto. III, Grey axinite from Nordmark; sp. gr. 3·28. IV, Axinite from Dannemora; sp. gr. 3·3. Analysis II is by A. Cleve, the others by Mauzelius:

| | $SiO_2$. | $B_2O_3$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MnO. | CaO. | MgO. | $K_2O$. | $Na_2O$. | $H_2O$. | F. | Total, less O for F. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I. | 42·40 | 4·88 | 17·26 | 1·33 | 4·27 | 6·97 | 19·53 | 1·30 | 0·21 | 0·25 | 1·90 | trace | 100·30 |
| II. | 42·55 | 4·20 | 16·37 | 3·79 | 4·06 | 7·69 | 19·28 | 1·02 | — | 0·10 | 1·33 | — | 100·39 |
| III. | 42·40 | 4·71 | 17·39 | 0·59 | 4·89 | 6·16 | 19·57 | 1·69 | 0·25 | 0·24 | 1·64 | 0·22 | 99·66 |
| IV. | 41·96 | 4·61 | 17·69 | 0·81 | 3·61 | 8·51 | 19·71 | 0·97 | not det. | | 1·93 | 1·11 | 100·44 |

The $Al_2O_3$ of I and III includes some $TiO_2$; the $H_2O$ in II is too low. Here $B : Si = 1 : 5$ (really 1 : 5·03, 1 : 5·85, 1 : 5·21, and 1 : 5·29 respectively), $R : Si = 1 : 2$, and $Si : O = 1 : 4$, when $R = (Al_{\frac{2}{3}},Fe,Ca \ldots H_2)$; from this follows the formula $BAl(SiO_4)_5R''_7$. Preference is, however, given to the basic metasilicate formula, $Al(BO_2)(SiO_3)_5R''_4$, as powdered axinite has an alkaline reaction; in this, boron being a negative element, $BO_2$ is considered as an acid radicle. Several of the more certain published analyses also give in the mean the ratio $B : Al : SiO_3 : (R'' + 2R''OH + 2AlO) = 1 : 1 : 5 : 4$. L. J. S.

**Edingtonite from Böhlet, Sweden.** By Otto Nordenskiöld (*Bull. soc. fran. min.*, 1895, **18**, 396—398; and *Geol. Fören. i Stockholm Förh.*, 1895, **17**, 597—600).—This zeolite, previously only known from Old Kilpatrick, in Dumbartonshire, was determined by Haidinger to be tetragonal and hemihedral. Examination of large crystals of a new find at the manganese mines at Böhlet, in Vestergötland, shows the mineral to be orthorhombic and hemihedral, with $a : b : c = 0·9872 : 1 : 0·6733$. There are perfect cleavages parallel to $m(110)$, $(mm' = 89° 16')$, and one less distinct parallel to $c(001)$. The plane of the optic axes is $b(010)$, and the acute negative bisectrix is perpendicular to $c(001)$; $2V_{Na} = 52° 55'$; sp. gr. 2·776. Detailed crystallographic and optical determinations are given. The axial ratios are compared with those of natrolite and scolecite. L. J. S.

**Analysis of a Variety of Ilmenite.** By George M. Peek (*Amer. Chem. J.*, 1897, **19**, 232).—The specimen examined was from

Bedford Co., Va. It occurs enclosed in veins of quartz, it cleaves well in one direction, and less readily in a second at an angle of 45°. Sp. gr. = 4·699; hardness 5·25. It is not magnetic. The crystals are probably tetragonal. Analyses gave

| $TiO_2$. | FeO. | MgO. | $SiO_2$. | Total. |
|---|---|---|---|---|
| 63·31 | 35·99 | 0·82 | 1·25 | 101·37 |

This approximates with the formula $Fe_2Ti_3O_8$. A. W. C.

**Synthetical Studies.** By Cornelius Doelter (*Jahrb. f. Min.*, 1897, i, 1—26)—Various minerals have been fused alone or with chlorides, fluorides, &c., and the fused mass allowed to cool slowly; the minerals thus formed in the glassy products vary considerably, and depend probably on the temperature at which solidification takes place, the action of the fluxes being mainly in lowering the temperature. At higher temperatures, olivine, leucite, augite, scapolite, and nephelite are formed, at lower temperatures, hornblende, mica, garnet, albite, and orthoclase. As a rule, orthosilicates seem to be the most stable, whilst metasilicates are easily altered into orthosilicates.

Micas when fused alone, usually give leucite and nephelite, but meroxene gives augite, spinel and scapolite. Tourmaline gives olivine and spinel, and, with calcium chloride and sodium fluoride, also melilite. Axinite and epidote give lime-augite and anorthite; epidote with fluorides gives anorthite, meionite, garnet, olivine, &c., and sometimes epidote recrystallises. Zoisite with chlorides gives garnet, olivine and anorthite. Hornblende gives augite, olivine, &c., and attempts to prepare hornblende by fusion usually result in these minerals being formed; but when the temperature is lowered to 500—700° by the addition of borax, &c., hornblende crystals can be produced by the fusion of powdered hornblende or of a mixture of the necessary oxides. Minerals of the scapolite group are frequently formed when various minerals and rocks are fused; meionite is obtained in good crystals by fusing a mixture having the composition of this mineral. Acmite is formed with magnetite and hæmatite by fusing $Na_2Fe_2Si_4O_{12}$. A mixture of $Al_2O_3 + 2SiO_2$ fused with fluorides gives mica, nephelite, leucite, scapolite, and felspars; the results of fusing various other mixtures are also described in detail. The significance of these and many other similar reactions are discussed in connection with the genesis of igneous rocks.

L. J. S.

**Analyses of Infusorial Earth.** By F. W. Smither (*Amer. Chem. J.*, 1897, 19, 235—236).—Analyses of three samples of infusorial earth, consisting almost entirely of shells, gave the following results:

| | $SiO_2$ amorphous. | $SiO_2$ cryst. | $TiO_2$. | $Fe_2O_3$. | $Al_2O_3$. | MgO. | CaO. | $OH_2$ at 100°. | Loss on ignition. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|
| Rappahannock | 65·83 | 14·65 | 0·40 | 2·34 | 4·17 | 0·71 | trace | 4·13 | 7·50 | 99·73 |
| Richmond...... | 51·67 | 23·56 | 0·64 | 2·79 | 10·25 | 0·69 | 0·27 | 4·73 | 5·45 | 100·05 |
| Patuxent......... | 48·58 | 35·23 | 0·60 | 1·20 | 5·20 | — | 0·25 | 5·09 | 4·22 | 100·37 |

A. W. C.

**An Alum Water from Lee Co., Virginia.** By L. E. Smoot (*Amer. Chem. J.*, 1897, 19, 234).—The water is odourless and colour-

less, with a decided acid reaction and strong taste of alum. The temperature of the spring is 70° F. composition:

| | $Al_2O_3$. | $Fe_2O_3$. | $Na_2O$. | $SO_3$. | $N_2O_5$. | $SiO_2$. | Total. |
|---|---|---|---|---|---|---|---|
| Grams per litre | 0·891 | 0·120 | 0·060 | 2·530 | 0·006 | 0·108 | 3·715 |

A. W. C.

## Physiological Chemistry.

**Digestibility of Cacao-butter and of Butter from Cow's Milk.** By BOUROT and FERDINAND JEAN (*Compt. rend.*, 1896, **123**, 587—590).—Cacao butter is used as a food in many countries, and the present experiments show that it has a high nutritive value; ordinary butter was digested to the extent of 95·8, and cacao-butter to that of 98 per cent.; in both cases, therefore, a very small residue of fat was found in the fæces. W. D. H.

**Effect of Fresh Thyroid and Iodothyrin on Metabolism.** By FRITZ VOIT (*Zeit. Biol.*, 1897, **35**, 116—154).—The experiments were carried out on dogs in the usual way; the ingesta and egesta were analysed, both while the animal was taking normal diet and diet to which was added either fresh thyroid or iodothyrin. The result produced by either addition was the same, namely, an increase in the quantity of urine and excretion of nitrogen, a deficit in nitrogenous equilibrium, a loss of weight, a loss of fat, and an increase of excretion of carbonic anhydride. If the animals were in a state of inanition, these results were more marked. A review of previous work on the subject is given. W. D. H.

**Source of Muscular Energy.** By J. B. AUGUSTE CHAUVEAU (*Compt. rend.*, 1896, **122**, 1303—1309).—By a comparison of the work and heat produced by contracting muscles, with the products of combustion, and the carbohydrate nutriment supplied to them, it is considered that the nature of the transformation of potential into actual energy is, as Lavoisier taught, combustion pure and simple.

W. D. H.

**Source of Muscular Energy.** By J. B. AUGUSTE CHAUVEAU and F. LAULANIÉ (*Compt. rend.*, 1896, **122**, 1244—1250).—Experiments were made on dogs and rabbits; the nutrition was either *nil* or abundance of carbohydrates. The muscles were excited to activity electrically, and the respiratory quotient determined before, during, and after, muscular work. The source of muscular energy is regarded as being always carbohydrate in nature, either from the store of glycogen in the body, or indirectly by a transformation of fat, or from the carbohydrate furnished directly to the muscles during absorption of food. W. D. H.

**Coagulating and Toxic Properties of the Liver.** By ALBERT MAIRET and VIRES (*Compt. rend.*, 1896, **123**, 1076—1078).—An aqueous extract of rabbit's liver was injected intravenously into other

rabbits, and found in certain doses to cause death; the blood was found to be coagulated in the heart and veins. By heating the extract, a coagulum is obtained; this contains the substance which produces the intravascular clotting; the filtrate is, however, still toxic, although it does not coagulate the blood. W. D. H.

**The Active Physiological Substances of the Suprarenal Gland.** By B. Moore (*J. Physiol.*, 1897, **21**, 382—389).—The active substance of the medulla is not catechol, or a derivative of catechol as Frænkel considers; neither is it identical with the chromogen originally described by Vulpian, for alcohol destroys the activity of the substance without affecting the reactions of the chromogen. It is suggested that the active substance is a pyridine derivative, possibly piperidine. The last named alkaloid certainly produces a great rise of blood pressure (see also Tunnicliffe, *Centr. Physiol.*, March 8th, 1897).

W. D. H.

**Thrombosin.** By C. D. Cramer (*Zeit. physiol. Chem.*, 1897, **23**, 74—86).—Schäfer and Hammarsten have previously expressed the opinion that Lilienfeld's thrombosin is nothing else but fibrinogen. The elementary analysis given in the present communication confirms this view. W. D. H.

**The Reaction of the Intestine in Relationship to Intestinal Digestion.** By B. Moore and D. P. Rockwood (*J. Physiol.*, 1897, **21**, 373—381).—Under normal conditions, the intestinal contents are not acid throughout, although in a few exceptional cases an undue amount of bacterial action may produce this result. The alkalinity is greater in herbivora than in carnivora, but in carnivora may be made to resemble that of herbivora by diet, for instance, feeding a dog on bread and water.

Fats induce an acid reaction throughout the greater part of the dog's intestine, but in rats and guinea pigs the contents remain alkaline. This is due to weak organic acids, which do not affect methyl-orange, but affect litmus.

Proteid (lean horseflesh) gives an acid reaction in the upper part of the intestine, and a faint alkaline reaction in the lower part in dog and cat, but in rats there is an alkaline reaction throughout.

The experiments indicate that, contrary to current theory, very little bacterial decomposition of carbohydrates takes place in the small intestine. Acidity begins in the cæcum. It is regarded as probable that the human intestine lies intermediate between that of carnivora and of herbivora. W. D. H.

**Comparison of the Diffusion into Serum, and Absorption by the Intestine, of Peptone and Glucose.** By E. Waymouth Reid (*J. Physiol.*, 1897, **21**, 408—425).—The diffusibility of peptone through parchment paper into serum is greater, and that of glucose slightly less, than into water. The absorption of glucose and peptone by the gut in different animals is not proportional to the extent of the absorbing surface.

The ratio of diffusion of glucose and of Grübler's peptone, through parchment paper into serum holding 0·1 per cent. of glucose in solution,

is not the ratio of the absorptions of these substances by the intestinal mucous membrane. The latter is slightly less permeable by glucose than by Grübler's peptone, whilst in the case of parchment paper it is the reverse.

The relation of diffusion of Grübler's and dialysed Witte's peptone through parchment paper into serum is also not the ratio of the absorptions of these substances in the gut. The latter is about equally permeable by both substances, while parchment paper is more permeable to Grübler's than to Witte's preparation. W. D. H.

**Permeability of Membranes for Putrefaction Processes.** By Hans Hensen (*Zeit. Biol.*, 1897, **35**, 101—115).—Bacteria can pass through the membranes (artificial and natural) used in diffusion experiments, even when they will not permit the passage of such substances as hæmoglobin. A membrane without such a disadvantage is still to be found. W. D. H.

**The Chemical Changes within the Organism of a Normal Animal.** By Maurice Kaufmann (*Bied. Centr.*, 1897, **26**, 25—26; from *Arch. Physiol.*, [v], **8**, 329—341).—In a dog fed with milk containing much cane-sugar, there was abundant deposition of fat, produced by the partial oxidation of proteids. The heat evolved amounted to one-eighth to one-fourth of the total amount of heat which the dog developed; most of the heat produced arose from the complete oxidation of the sugar in the blood. In the case of carnivorous animals, only a very slight amount of sugar is converted into fat, whilst in vegetarians and animals which consume mixed food, sugar has a direct and essential share in producing fat. A portion of the sugar is deposited in the liver and muscles as glycogen.

When much proteid is consumed, it is decomposed into fat, carbonic anhydride, urea, and water, the fat being partly deposited and partly converted, first into sugar, then into carbonic anhydride. Most of the heat results from the primary oxidation of the proteids.

Fat, when consumed in conjunction with plenty of proteid or carbohydrate, is completely or partly deposited. It is, however, partly oxidised when the supply of carbohydrates in the body is diminished, as after 24 hours' fasting.

When food is withheld, the animal lives on reserve carbohydrates. Although the amount reserved is small, glycogen is found in the muscles after 10—15 days' fasting. The proteids and the fat are first converted into sugar, then burnt. There are three periods of hunger: first the supply of carbohydrates is diminished, then the loss of carbohydrates is made up from proteids and fat, the co-efficient of respiration sinking to 0·66. In the third period, sugar is produced in exactly the same proportion as it is burnt, that is to say, the animal lives on the decomposition of proteids and fat. The co-efficient of respiration is at this time 0·74. The proteids furnish one-sixth of the total heat at the beginning, and one-third at the end, of the period of fasting.

N. H. J. M.

**Decomposition of Proteid in the Human Organism.** By Eyvind Bödtker (*Bied. Centr.*, 1897, **26**, 130; from *Centr. Med. Wiss.*,

34, 354).—In healthy adults, the urea excreted contained from 88·44 to 91·39 per cent. of the total nitrogen. The uric acid nitrogen amounted, on the average, to 1·5 per cent. of the total nitrogen. There is no constant relation between the percentage of nitrogen as uric acid, and as ammonia, and the total nitrogen. The average amount of ammoniacal nitrogen is 4 per cent. of the total. In children, the relation of urea and uric acid is about the same as in adults, but the ammoniacal nitrogen is usually higher (4 up to 9 per cent.). In slight cases of diabetes, the urea nitrogen is about 87 per cent., whilst the nitrogen as ammonia rises to over 13 per cent. The effect of other diseases on the form in which nitrogen is excreted was investigated.

N. H. J. M.

**Transformation of Fat into Carbohydrate in the Organism.** By J. B. AUGUSTE CHAUVEAU (*Compt. rend.*, 1896, **122**, 1098—1103).—In a starving animal, and during hibernation, the sugar which still persists in the blood must originate from either fat or proteid. Further, in hibernation, Regnault and Reiset showed that the respiratory quotient was very low, and the great excess of oxygen retained over carbonic anhydride given out leads to an actual increase of weight of the animal, but it loses its fat. W. D. H.

**Formation of Nuclein in Mammals.** By RICHARD BURIÁN and HEINRICH SCHUR (*Zeit. physiol. Chem.*, 1897, **23**, 55—73).—In connection with the probable origin of nuclein in the body, the question specially investigated in the present research is whether the administration of xanthine bases leads to the formation of nuclein. The experiments recorded on rabbits and dogs show that the bases can be formed in the body from other nitrogenous material, but mainly negative results were obtained relating to the special point investigated.

W. D. H.

**Fat Estimation.** By FR. N. SCHULZ (*Pflüger's Archiv.*, 1897, **66**, 145—166).—Dormeyer's digestion method of estimating fat in muscle can be applied with advantage to other tissues and organs. Mere inspection is untrustworthy in the formation of an opinion as to the amount of fat in a starving animal. An extended period of inanition is required to make an animal fat free, or at least to bring it to the lowest limit of the percentage of fat observed. The amount of nitrogen of the different dry, fat-free organs is about the same. The relative amount of cholesterol rises in the organs ; this may be because this substance is not altered by hunger as fat is. W. D. H.

**"Oxidation-ferments" of the Tissues.** By ERNST L. SALKOWSKI and KATSUSABURŌ YAMAGIWA (*Virchow's Archiv.*, 1897, **147**, 1—23).—It was shown by Jaquet (*Arch. exp. Path. Pharm.*, **29**, 386) that the tissues have the power of oxidising at the body temperature such substances as benzylic alcohol and salicylaldehyde. This does not depend on the life of the protoplasm, but on the presence of a soluble ferment. which is destroyed by boiling, and by the prolonged action of alcohol. The present research shows that the blood has the same power, Extracts of various organs act, however, with different degrees of oxidising power, as estimated by the amount of salicylic acid formed

from salicylaldehyde. The liver is the most powerful; and if its power is put at 100, the power of the spleen is 80·4; of the kidneys, 15·5; of the pancreas, 2·0; and of the muscles, 1·0. W. D. H.

**Non-putrescibility of Blood rendered Incoagulable by Leech-extract.** By Bosc and Delezenne (*Compt. rend.*, 1896, **123**, 465—467, 500—503).—Shed blood, which is kept fluid by a previous intravenous injection of leech-extract, does not putrefy readily. This is not due to the presence of any antiseptic substance in the extract, nor to an increased phagocytic action of the leucocytes, for the blood remains unputrefied after the death of the white corpuscles. The extract perhaps provokes such secretions from the corpuscles as increase the bactericidal power of the blood. In fact, the injection of leech-extract confers immunity on the animals to certain experimental infections. W. D. H.

**Pigments of Decapod Crustacea.** By M. I. Newbiggin (*J. Physiol.*, 1897, **21**, 237—257).—The animals investigated were the common lobster, *Nephrops*, the Norway lobster, and *Astacus nobilis*, the red-clawed crayfish.

In their shells, hypodermis, and ova there is a red lipochrome pigment. In shell and hypodermis this is either accompanied by a small amount of a yellow pigment, or more probably the red pigment is unstable and is converted by certain reagents, especially under the influence of heat, into a yellow pigment. The yellow pigment is identical with that occurring in the digestive gland, and is in part eliminated with the fæces.

The red lipochrome readily forms combinations with alkalis and alkaline earths; the compounds so formed are orange, and almost insoluble in alcohol. As the undecalcified shell of *Nephrops* is orange and yields like pigment to cold alcohol, whilst the decalcified shell is pink and yields its pigment readily to alcohol, it is probable that, in a shell, the pigment is present in combination with lime. The deep sea crustacea and the more delicate surface forms have but little lime in their cuticle, and are deep red.

The red lipochrome unites also with an organic base apparently derived from the muscle, and thus gives rise to the blue pigment of these animals.

The yellow hepatochrome of the liver appears to be the central pigment of the group; this may become modified to form the red lipochrome of the shell, or the orange pigment of the shell if it unites with lime. If the red lipochrome unites with the organic base, the blue is formed, and a mixture of the blue with unaltered yellow gives rise to green. W. D. H.

**Non-occurrence of Argon in the Colouring Matter of the Blood.** By J. Zaleski (*Ber.*, 1897, **30**, 965—969).—The gas obtained on burning the colouring matter of the blood with copper oxide was freed from nitrogen by means of magnesium or lithium, a modified form of the Schlœsing apparatus being used for the purpose; the residual gas, however, in no case showed the characteristic spectra of argon. J. F. T.

**Biological Relation of Chlorophyll and Hæmoglobin.** By MARCELLUS NENCKI (*Ber.*, **29**, 2877—2883).—Schunck and Marchlewski (*Annalen*, **290**, 306) have shown that *phylloporphyrin*, $C_{16}H_{18}N_2O$, a substance obtained from chlorophyll, is nearly related to hæmatoporphyrin, $C_{16}H_{18}N_2O_3$; hæmin and phyllotaonin are also similar and form similar compounds, this similarity extending to spectroscopic appearances. It appears, therefore, that the basis of blood pigment and leaf pigment is the same; in view of the Darwinian hypothesis, and the essential unity of living things, such a discovery is of value. The rest of the paper deals with the biological importance of the question, and other examples of the universal application of certain chemico-biological laws are taken from different parts of the animal and vegetable kingdom. W. D. H.

**Composition and Nutritive Value of Sardines Preserved in Oil.** By DOMENICO MARTELLI (*Staz. Sper. Agrar.*, 1895, **28**, 225—235).—The following percentage results were obtained with sardines from (1) Sicily, (2) Tunis, and (3) Sardinia:

| | Water. | Fat. | Nitrogen as Proteids. | $NH_3$. | Ash. | CaO. | MgO. | $P_2O_5$. | $SO_3$. | Cl. |
|---|---|---|---|---|---|---|---|---|---|---|
| 1. | 50·16 | 12·68 | 4·302 | 0·168 | 7·51 | 0·09 | 0·19 | 0·61 | 0·03 | 3·77 |
| 2. | 50·36 | 13·07 | 4·075 | 0·193 | 7·85 | 0·14 | 0·21 | 0·58 | 0·02 | 4·08 |
| 3. | 40·66 | 23·75 | 3·836 | 0·252 | 8·98 | 0·07 | 0·20 | 0·53 | 0·01 | 4·73 |

A part of the organic nitrogen (given as "nitrogen as proteids") is probably present in the form of amides or amido-acids.

Calculating the nutritive value of the fish by König's method, taking the value of the proteids and fat respectively as 5 and 3 times that of carbohydrates, 1 kilogram of each of the three samples is found to contain the following numbers of units of nutritive value: (1) 1725, (2) 1666, and (3) 1900. N. H. J. M.

**Formation of Urea by Oxidation.** By FRANZ HOFMEISTER (*Chem. Centr.*, 1896, ii, 389—390; from *Arch. exp. Path. Pharm.*, **37**, 426—444).—With the exception of Béchamp's unrecognised attempts, the formation of urea from albumin or other nitrogenous substances has not been proved. Schultzen and Nencki showed that the nitrogen of amido-acids is excreted almost entirely as urea, and Knieriem proved that even ammonium salts are changed into urea in the animal organism. The most general view, therefore, of the origin of urea is that the final products of oxidation, carbonic anhydride, and ammonia form urea with elimination of water. Drechsel has shown that, by hydrolysis, only a small portion of the nitrogen of albumin is eliminated as urea.

By oxidation of a great variety of substances with potassium permanganate, the author has obtained urea, often even in considerable quantity. The substance was oxidised in aqueous solution with addition of ammonia and ammonium sulphate, by means of a quantity of potassium permanganate nearly sufficient to convert it into carbonic anhydride, water, and urea. Decolorisation took place in times varying from a quarter of an hour to several days. The liquid was then filtered, the filtrate evaporated almost to dryness at 40—50°, and the

crystalline mass digested 10—12 hours with 96 per cent. alcohol. The filtrate was evaporated, and to the residue dissolved in alcohol half its volume of ether was added and the whole then filtered and evaporated. The presence of urea in the residue was proved by preparation of the nitrate and its microscopical examination, or, when in sufficient quantity, by determination of the melting point and estimation of the nitrogen.

Urea was proved to have been formed in the cases of hydrocyanic acid, thiocyanic acid, formamide, glycocine (3 grams of urea nitrate from 10 grams of glycocine), oxamic acid (0·7 gram of nitrate from 10 grams of acid), aspartic acid, asparagine, leucine (0·2 gram nitrate from 5 grams of leucine), gelatin, egg-albumin (2 grams of nitrate from 39 grams of albumin), methylic alcohol, ethylene glycol, glycollic acid, acetone, lactic acid, malic acid, tartaric acid (0·7 gram of nitrate from 20 grams of acid), and pyrogallol. No urea was formed from ethylamine, acetonitrile, acetamide, oxamide, succinamide, formaldehyde, formic acid, carbonic acid (ammonium carbonate containing carbamate), ethylic alcohol, acetaldehyde, acetic acid, glyoxal, propionic acid, malonic acid, glyceric acid, butyric acid, succinic acid, or grape sugar.

This synthesis of urea depends on the union of $NH_2-$ and $CO-$ groups, hence compounds containing no nitrogen may form urea by the help of ammonia. The experiments show that the groups $CH_3\cdot C\equiv$ and $\equiv C\cdot COOH$ cannot yield urea, whilst $-CH\cdot NH_2, -COOH$, and $-CH\cdot OH, -COOH$ very easily form it, and that the groups $-CN$ and $-CH_2\cdot OH$ can furnish the CO groups necessary for the formation of urea only when present in the simplest carbon compounds, such as formamide, oxamic acid, hydrocyanic acid, methylic alcohol, or ethylene glycol.

The substances which, on oxidation with permanganate, did not form urea, such as acetamide and oxamide, are also unchanged in the animal organism, whereas oxamic acid which yielded urea is also oxidised to urea in the body without previous formation of oxalate. It is still uncertain, however, as to whether this natural synthesis of urea is one of oxidation and elimination of water, but such an assumption does away with the necessity of attributing a special function to the liver, as this organ is found to be especially capable of oxidising fatty substances. The author's observation that the liver contains no cyanic acid is opposed to the view that the formation of urea is analogous to its production from ammonium cyanate. E. W. W.

**Excretion of Nitrogen by the Intestine.** By JIRO TSUBOI (*Zeit. Biol.*, 1897, **35**, 68—93).—Consideration of results of previous workers, and the present examination of the fæces in dogs, show that the amount of nitrogen that leaves the body by the intestine is by no means negligible, and varies with diet. Less proteid is assimilated when it is mixed with fat than when it is mixed with starch. This fact must be taken into consideration in all studies on metabolic phenomena, even if the products of nitrogenous metabolism in the fæces are scanty. W. D. H.

**The Fat of Ovarian Dermoid Cysts.** By ERNST LUDWIG (*Zeit. physiol. Chem.*, 1897, **23**, 38—39).—From fat obtained from the interior of numerous dermoid cysts of the ovary, cetylic alcohol was

separated, and also a new oily substance, similar in many points to cholesterol. W. D. H.

**The Fat of Ovarian Dermoid Cysts.** By RICHARD VON ZEYNEK (*Zeit. physiol. Chem.*, 1897, 23, 40—54).—A fuller investigation of the cholesterol-like substance alluded to in the preceding abstract. By fractional distillation, it was separated into five fractions differing in their solubilities, optical activity, and percentage composition. Attempts to make crystalline compounds, however, failed. No further conclusion than that the substance has some resemblance to cholesterol is arrived at. W. D. H.

**A Remarkable Case of Alcaptonuria: Estimation of Alcapton (Homogentisic Acid).** By GEORGES DENIGÈS (*J. Pharm.*, 1897, [vi], 5, 50—54).—In a case of facial and sciatic neuralgia, it was found that, although polarimetric examination of the urine gave negative results, and the urine did not ferment in presence of yeast, the quantity of glucose indicated by Fehling's test was considerable.

In 1859, Bœdecker separated from urine of a similar nature, a substance, alcapton, which was shown by Wolkow and Baumann to be a homogentisic acid, $C_6H_3(OH)_2 \cdot CH_2 \cdot COOH$ (Abstr., 1891, ii, 1128).

The author succeeded in separating a quantity of this substance from the sample of urine in question. He further succeeded in showing that the quantity secreted is increased under meat diet, and is roughly proportional to the quantity of urea present. This confirms Baumann's theory that alcapton is formed by the breaking down of tyrosine.

Alcapton may be estimated in the following manner: 10 c.c. of filtered urine, 10 c.c. of ammonia solution, and 20 c.c. of decinormal silver nitrate solution are placed together in a flask for 5 minutes. Five drops of calcium chloride solution and 0·5 c.c. of ammonium carbonate solution are added; the solution is made up to 50 c.c., and filtered. The silver is estimated in half the filtrate. One molecule of alcapton, $C_8H_8O_4$, reduces 4 atoms of silver. M. W. T.

**Osmotic Properties of Cells in their Bearing on Toxicology and Pharmacy.** By ERNST OVERTON (*Zeit. physikal. Chem.*, 1897, 22, 189—209).—The author considers more especially the peculiar selective influence of some classes of poisons and medicines, as a consequence of which only one class of cells is especially affected, the remainder being either not affected or only indirectly. As in some cases the gain or loss of a compound by the cell protoplasm is not a purely osmotic process, the local action could be explained by the assumption that the poison, &c., only enters the particular cells which exhibit the alteration of function. This, however, does not appear to be the case in the majority of cases, and many toxic compounds including the anæsthetics, hypnotics, and antipyretics readily pass through both plant and animal membranes, so that in their case the passage is solely osmotic. The local action is hence most probably due to the fact that the functional activity of the one class of cells is materially influenced by a much smaller concentration of the particular compound in its cell-fluid than is the case with

the other cells. In some cases, however, this does not appear to be the explanation; for example, the action of barium and potassium salts on the cardiac muscles, and such cases require further research. L. M. J.

## Chemistry of Vegetable Physiology and Agriculture.

**The Coloration of the Sap of Beetroot and the Soluble Oxidising Ferments.** By GABRIEL BERTRAND (*Bied. Centr.*, 1897, **26**, 60—62; from *Bull. Assoc. Chim.*, **14**, 19, and *Neue Zeit. Rübenzuck.-Ind.*, 1896, 253).—The coloration of beetroot sap when exposed to air is due to the action of a soluble ferment belonging to the new group of oxydases. These ferments are readily detected by means of an alcoholic solution of guaiacum resin, a drop of which applied to vegetable sap containing the ferment produces a blue coloration.

The reddening, and subsequent blackening, of beetroot sap, is due to the oxidation of tyrosine, by the combined action of air and an oxydase (tyrosinase). Laccase (another oxydase) has no effect on tyrosine. Whilst tyrosinase is destroyed by heating for 12 minutes at 60—70°, laccase is not entirely destroyed after 20 hours' heating.

Tyrosinase was also isolated from the tubers of dahlia and from *Russula nigrans.* N. H. J. M.

**Action of Ammonium Nitrate on Aspergillus niger.** By CHARLES TANRET (*J. Pharm.*, 1897, [vi], **5**, 5—8).—When *Aspergillus niger* is cultivated on the surface of a liquid containing 0·25 gram of ammonium nitrate per 100 c.c., the mycelium develops rapidly, and bears spores in less than 24 hours. If two or three times the quantity of ammonium nitrate is taken, the mycelium is formed as before, and reaches enormous proportions; no reproductive organs are, however, produced. In the latter case, the liquid is found to contain free nitric acid, whilst the body of the mycelium contains starch. M. W. T.

**Action of Carbonic Anhydride on the Protoplasm of Living Plant Cells.** By G. LOPRIORE (*Bied. Centr.*, 1897, **26**, 102—104; from *Jahrb. wiss. Bot.*, 1895, **28**, 531—626; and *Bot. Centr.*, 1896, **66**, 15).—Pure carbonic anhydride has no permanently injurious effect on the streaming movement of protoplasma, but only momentarily hinders it. When 20 or 10 ten per cent. of oxygen is mixed with the gas, the movement of the protoplasma gradually accommodates itself to the large amount of carbonic anhydride, and is then no longer checked in the almost pure gas.

Pure oxygen sometimes accelerates the streaming, but not to the extent often supposed. Pure hydrogen often quickens the movement at first, but afterwards retards it.

Mucor spores cannot germinate in pure carbonic anhydride, but are however, not destroyed by being kept 3 months in the gas. Germination is considerably retarded, but not injured by pure carbonic

anhydride mixed with 70—90 per cent. of oxygen. With less oxygen, the growth of the mycelium is arrested, and there is no formation of sporangium.

The increase of yeast is checked in pure carbonic anhydride, but proceeds when the gas is replaced by air. *Mycoderma cerevisiæ,* however, lost the power of increasing when kept for 12 hours in the pure gas.

Pollen grains vary in their behaviour towards carbonic anhydride according to the kind of plant; some form blistered protuberances which burst after a short time, whilst others do not germinate, or at once burst. Pollen tubes generally burst in pure or diluted carbonic anhydride, and even 1—10 per cent. of the gas considerably hinders growth.

N. H. J. M.

**The Amount of Iodine in certain Algæ.** By ESCHLE (*Zeit. physiol. Chem.*, 1897, **23**, 30—37).—In both *Fucus vesiculosus* and *Laminaria digitata*, the iodine is almost exclusively in the form of an organic compound. The nature of the substance is uncertain, but, from a study of its solubilities, it appears to be a mixture of several substances.

W. D. H.

**Relation between Lime and the Carbohydrates in Plants.** By P. GROOM (*Bied. Centr.*, 1897, **26**, 136—137; from *Naturw. Rundschau.*, 1896, 931).—The accumulation of carbohydrates in plants when calcium is deficient is attributed to the presence of acid oxalate, which prevents the conversion of starch into sugar. Direct experiments showed that hydrogen potassium oxalate retards the action of diastase on starch. The effect of hydrogen potassium oxalate on living plants was first to promote the accumulation of starch, owing to its non-conversion into sugar, and then to retard starch formation, and probably also assimilation of carbon. The final effect of the accumulation of the oxalate was the death of the protoplasm.

N. H. J. M.

**Solubility of the Red Colouring Matter of Grapes: Sterilisation of the Musts of Fruits.** By AUGUSTE ROSENSTIEHL (*Compt. rend.*, 1897, **124**, 566—569).—The red colouring matter of the grape, contrary to the general belief, is soluble in grape juice when the latter is heated, even in absence of alcohol. The solution takes place more rapidly the higher the temperature, and requires about 5 hours at 70°. The same phenomenon is observed with other fruits containing a red colouring matter.

These colouring matters are very unstable, and are decolorised by contact with tin, bronze, and brass, but are only slightly affected by copper. Exposure to air at 50° renders them quite insoluble, even in alcohol, and it follows that exclusion of air is indispensable if the red colouring matter of the grape and other fruits is to remain in solution. The musts of the grape, and of other fruits, when preserved from contact with air, retain the agreeable taste of the fresh fruit. In absence of air, they can be heated for a long time and repeatedly at 45—50° without undergoing the change known as "goût de cuit." Moreover, repeated heating even at this low temperature results in sterilisation of the musts, which can afterwards be

kept for weeks in the ordinary vessels used for storing wine without undergoing any alteration and without any loss of the colour, odour, or taste of the fresh fruit. C. H. B.

**Nutritive Value of Beetroot Leaves.** By FRANZ LEHMANN (*Bied. Centr.*, 1897, **26**, 96—99; from *Hannov. Land. u. Forstwirtsch Zeit.*, 1896, No. 44).—Feeding experiments were made with four sheep to ascertain the value of sour beetroot leaves. The following average amounts of constituents digested in (1) unwashed and (2) washed leaves are given, and compared with (3) mangolds:

| | Organic matter. | Proteids. | Fat. | Carbohydrates. |
|---|---|---|---|---|
| 1. Beetroot leaves | 11·12 | 0·17 | 0·34 | 9·69 |
| 2. Beetroot leaves | 10·12 | — | 0·25 | 9·17 |
| 3. Mangolds | 9·83 | 0·15 | 0·05 | 8·32 |

The nutritive value of the leaves, therefore, resembles that of mangolds.

In the process of washing, the leaves lost the following percentage amounts of each constituent: organic matter, 9·0; crude proteid, 36·9; fat, 26·5; crude fibre and nitrogen-free extract, 5·4. The loss of nitrogenous matter is very high, but as the sour leaves contain little digestible proteid (consisting chiefly of undigestible proteids and amides) there is not much actual loss. N. H. J. M.

**Preservation and Composition of Hops.** By JOHANNES BEHRENS (*Bied. Centr.*, 1897, **26**, 54—57; from *Wochenschr. f. Bierbrauerei*, 1896).—Among the organisms isolated by the author from hops were a bacillus (*B. lupuliperda*) which produces a green fluorescence in suitable solutions, and forms trimethylamine from certain constituents of hops (compare this vol., ii, 115), a kind of *Aspergillus*, and various yeasts. The spontaneous heating of hops is due to microorganisms, but not always to the same kind. The mould fungi destroy the acids of the hops and produce carbonates from the organic salts.

The following analysis of hops is given. The numbers show the percentage amounts in dry substance free from sand:

| Nitrogen | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Total. | Proteid. | Soluble in water. | Ether extract. | Light petroleum extract. | Aqueous extract. | Tannin. | Ash. | $HNO_3$. |
| 3·26 | 2·24 | 1·58 | 17·15 | 15·49 | 24·83 | 3·59 | 7·66 | trace. |

The fresh hops contained water (8·12) and sand (1·65 per cent.).

The coloration of hops (brown or red) is due to insufficient acidity and may be produced by adding alkali. The amount of acid in hops varies with the kind, season, &c.; it raises the acidity of the wort and so essentially influences the process of fermentation. The presence of acid is practically without effect in the sterilisation of the wort. The sulphurisation of hops is effective in improving the colour of hops; it has no effect on their hygroscopic properties. As regards the disinfecting power of sulphurous acid, it was found that whilst an extract of hops which had not been sulphurised soon produced a luxuriant mould vegetation, a similar extract of hops which had been so treated contained only very few and quite sterile mycelium flakes. The effect of sulphurous acid was, therefore, not sterilisation in the ordinary sense,

but to render the hops more or less incapable of becoming infected, a far more important result. N. H. J. M.

**Ordinary and Dried Superphosphate.** By LOUIS DECOUX and LOUIS DRUMEL (*Bied. Centr.*, 1897, 26, 79—80; from *L'ingénieur agric.*, 1896, 110).—The results of field experiments in which barley was manured with sodium nitrate alone and in conjunction with ordinary and dried superphosphate respectively, indicated that the ordinary superphosphate was more effective than the dried. The addition of sodium nitrate was advantageous. N. H. J. M.

**Effect of Potash Manuring on the Quality of Brewing Barley.** By THEODOR REMY (*Bied. Centr.*, 1897, 26, 15—17; from *Wochenschr. f. Braueri*, 1896, No. 41).—The following conclusions are given with reserve, owing to the limited number of samples available for examination. There is no indication of a favourable effect due to large applications of potash, and potash manuring can only be insisted on when the potash in the soil is insufficient for good crops, and then only with the view of increasing production. On the other hand, the unfavourable effect of a heavy application of potash (in increasing the percentage of nitrogen) is so slight that it need hardly be considered. Too much hope should not be placed in potash as a specific means of producing better barley for brewing. N. H. J. M.

**The Rôle of Fat in Manures.** By J. HANS VOGEL (*Bied. Centr.*, 1897, 26, 128—129; from *Deut. landw. Presse.*, 1896, No. 74).—Stable manure, green manure, guano, and crude bone meal contain 0·5—2 per cent. of fat, whilst manure prepared from human excrement contains from 8—9 per cent. Fat would be injurious when, for instance, it is important for the nitrogenous matter to become quickly available to the plant. This, however, does not occur, as in such cases manures free from fat would be applied. Fat would be useful in delaying the decomposition of nitrogenous matter applied in the autumn. In the case of human excrement, the fat slowly decomposes during the autumn but this ceases in winter; in the spring, the fat gradually decomposes, liberating at the same time the nitrogenous matter just at the time it is required for the crop. Loss of nitrogen is thus prevented. The presence of fat is particularly favourable in the case of light, sandy soils. N. H. J. M.

**Action of Potassium Salts on different kinds of Soil** (*Bied. Centr.*, 1897, 26, 9—14; from *Arbeiten d. deut. Landw. Ges.*, Heft. 20). —I. *Action of Potassium Salts on Sandy Soil* (MAX MAERCKER).—A number of pot experiments were made with a light sandy soil mixed with 2·5 per cent. of peat, together with different potash manures. The results of the first series of experiments made with lucerne, without potash, with kainite, carnallite and "Hartsalz" (containing 15 per cent. of potash) showed a great increase of produce under the influence of potash. The effect of the three salts was about equal. Potassium carbonate was, however, more effective than any of the three. Sodium carbonate, used in small quantity, gave a slight increase of produce, whilst a larger quantity diminished the yield. The same potassium salts gave similar results with white mustard; sodium

carbonate and chloride, even in small quantities, were injurious. With potatoes, the potash manures had relatively little effect, and the percentage of starch was not materially increased. In an experiment with grasses and *Leguminosæ* (mixed), it was found that where large amounts of potash were given, the produce contained so much potash that the residue in the soil was about the same as when less was applied, and it is concluded that meadows should receive potash every year. The relation of grasses to leguminous plants increased under the influence of potash manure.

II. *Action of Potassium Salts on Peaty Soil* (BRUNO TACKE).—Five series of pot experiments are described. The peaty soil received burnt lime (15 grams), basic slag (containing $P_2O_5 = 2$ and 3 grams), and sodium nitrate (0·8 and 1·5 gram of nitrogen in each pot). Kainite, carnallite, potassium sulphate, "Hartsalz," from Solvayhall, near Bernburg, and potassium magnesium carbonate were added in amounts containing 0·375, 0·5, and 0·625 gram of potash (corresponding with about 75, 125, and 175 kilos. per hectare). The plants selected were oats, wheat, barley, and white mustard.

The results of the experiments showed that the peaty oils required potash in order to give satisfactory results. The grain crops generally had feeble stems unless sufficiently supplied with potash; but large amounts of potash did not materially increase the yield as compared with the less amounts.

The effect of potash on the amount of potash in the produce was very variable. In some cases, the percentage of potash in the produce was about the same when potash was applied as when it was not, and sometimes it was even less. The straw was frequently richer in potash, the grain less frequently, when manured with potash. The percentage of phosphoric acid and nitrogen was generally unmistakably diminished in the plants manured with potash. In rye and barley, the starch was considerably increased under the influence of potash.

In some cases, the soil which had received potash became poorer in potash than it was originally, owing to increased root development under the influence of the manure. N. H. J. M.

## Analytical Chemistry.

**Barium Thiosulphate as Basis for Iodimetry.** By M. MUTNIANSKI (*Zeit. anal. Chem.*, 1897, 36, 220—221. See also Plimpton and Chorley, Trans., 1895, p. 314).—The solubility of barium thiosulphate at 17·5° is such that a saturated solution, prepared by shaking an excess of the salt for 15 minutes with water of that temperature, is of exactly N/100 strength. Such a solution deposits none of the salt when kept for several days at 15°. The barium thiosulphate is prepared by mixing hot concentrated solutions of 5 parts of sodium thiosulphate and 4 parts of barium chloride, and washing the precipitate, first with warm, then with cold water, with 95 per cent. alcohol, and finally with ether. Air drying for an hour suffices to render it fit for use. A

convenient starch indicator is prepared by triturating 5 grams of potato starch and 0·01 gram of mercuric iodide with 30 c.c. of cold water, and pouring the mixture into a litre of boiling water. After boiling for 3 minutes, it is allowed to cool. The clarified solution retains its sensitiveness (1 part of iodine in 3,500,000) for years. M. J. S.

**Rapid Estimation of Organic Nitrogen.** By LÉONARD (*Chem. Centr.*, 1896, i, 573; from *Rev. Chim. anal. appl.*, 1895, 285).—Ten c.c. of milk or urine is introduced into a long-necked 300 c.c. flask, mixed with 1 gram of dried copper sulphate, 1 gram of dried sodium phosphate, and 10 c.c. of strong sulphuric acid, and boiled until it becomes quite clear and green; when cold, the contents are transferred to a 100 c.c. measuring flask, supersaturated with aqueous soda, and the precipitated copper hydroxide redissolved by adding 20 c.c. of an alkaline solution of Rochelle salt. After making up to the mark, an aliquot part of the liquid is removed with a pipette, and the nitrogen in it is estimated either by distilling off the ammonia or by measuring the volume of nitrogen given off on adding an alkaline solution of bromine. L. DE K.

**Estimation of Ammonia in Animal Secretions and Tissues.** By MARCELLUS NENCKI and J. ZALESKI (*Chem. Centr.*, 1896, 1, 510—511; from *Arch. exp. Pathol. und Pharm.*, **36**, 385—394).—The finely divided matter, or the liquid, is distilled under diminished pressure at a temperature not exceeding 35°, the ammonia being liberated by means of limewater, or sometimes by milk of lime. The distillate is collected in a specially constructed bulb-tube containing standard sulphuric acid, the excess of which is afterwards titrated with standard soda, using methyl-orange as indicator. L. DE K.

**Microchemical Reaction for Nitric Acid.** By REINHARD BRAUNS (*Jahrb. f. Min.*, 1897, 1, 73).—Behrens' methods of first reducing the nitrate to nitrite or to ammonia are not direct, and not always applicable. The author suggests the following. A solution of nitrate gives, with barium chloride, sharply developed, regular octahedra of the sparingly soluble barium nitrate. L. J. S.

**Estimation of Very Small Quantities of Nitrous Acid.** By LUIGI ZAMBELLI (*Chem. Centr.*, 1896, 1, 1283; from *Mon. Sci.*, [iv], **10**, 351).—The reagent is prepared by dissolving 2 grams of sulphanilide and 2 grams of phenol in 25 c.c. of sulphuric acid mixed with 25 c.c. of water; the syrupy liquid thus obtained is at once ready for use. The liquid to be tested is put into a stoppered cylinder, mixed with 2 or 3 c.c. of the reagent, and after 10 or 15 minutes it is rendered alkaline with ammonia. If nitrites be present, a yellow coloration will make its appearance, which may be matched by using a solution of silver nitrite of known strength, and the amount of nitrous acid thus estimated. L. DE K.

**Estimation of Phosphorus in Steel and Cast Iron.** By GEORGE AUCHY (*J. Amer. Chem. Soc.*, 1896, **18**, 955—970).—The author recommends the following slight modification of Emmerton's reduction process. The yellow precipitate obtained by treating the nitric acid

solution of iron with ammonium molybdate and ammonium nitrate is dissolved in as small a quantity of ammonia as possible and poured back into the 8-oz. Erlenmeyer precipitation flask; 25 c.c. of dilute sulphuric acid (1 : 2) is added and then 5 grams of zinc, the flask being heated gently for 5 minutes or longer until the zinc is nearly dissolved. A little sodium carbonate is now added, and when effervescence has nearly ceased, the flask is corked and allowed to cool; the solution is filtered from the undissolved zinc through a little cotton wool in a Hirsch funnel of the smallest size, using the pump, and the flask is rinsed three times with cold water, the filtrate being titrated without delay by means of potassium permanganate. The author has proved, by a large number of experiments, that the molybdenum compound corresponds with the formula $Mo_{12}O_{19}$, although this at first may have been $Mo_2O_3$, which gets oxidised by filtering and dilution.

It sometimes happens that a portion of the yellow precipitate again separates on adding the sulphuric acid, but this may be ignored as it gradually becomes reduced and passes into solution. L. DE K.

**Citrate-solubility of Phosphoric Acid.** By ARMAND D. HERCZFELDER (*Zeit. angw. Chem.*, 1897, 73—77).—When treating basic slags with Wagner's citric acid solution, a portion of the acid is liable to be precipitated as calcium citrate. Being thus deprived of some of its solvent, part of the phosphoric acid may also be precipitated as ferric phosphate, and thus render the results too low.

The liquid should, therefore, not remain too long in contact with the sample, and must be soon filtered off. Any precipitate which may form afterwards must be redissolved by adding hydrochloric acid.

L. DE K.

**Citrate-soluble Phosphoric Acid in Basic Slags.** By MAX PASSON (*Zeit. angw. Chem.*, 1897, 82—84).—This is an attempt, partly successful, to calculate the amount of citrate-soluble phosphoric acid from the total citrate-soluble matter, the insoluble portion of the basic slags being collected on a weighed filter and weighed. Further experiments will, however, have to be made. L. DE K.

**Modification of the Method of Estimating the Soluble Phosphoric Acid in Basic Slag.** By GIOVANNI SANI (*Staz. Sper. Agrar.*, 1895, **28**, 275—276).—The substance (5 grams), mixed with water (100 c.c.), is treated with 10 per cent. citric acid, then with ammonium citrate (official solution, 200 c.c.) and heated on a water bath for an hour, keeping the mixture carefully stirred. It is then diluted to 500 c.c., and the process continued according to the official method. The results of analysis of two samples made by this modification of the official method, and by Wagner's method, are given, showing close agreement. N. H. J. M.

**Reinsch's Test for Arsenic and Antimony.** By JAMES L. HOWE and PAUL S. MERTINS (*J. Amer. Chem. Soc.*, 1896, **18**, 953—955).—The authors prefer the Reinsch's copper test for arsenic to using the Marsh's apparatus, as it does not require the destruction of organic tissues, and will still show the presence of one-millionth part of dissolved arsenic. When the copper is heated in a glass tube, the arsenic yields the charac-

teristic sublimate of arsenious acid, appearing as brilliant octahedra under the microscope. If it is not a case of arsenical but of antimonial poisoning, the slowly forming deposit on the copper will be of a decidedly violet tint, very distinct from the iron-grey deposit of arsenic; moreover, the sublimate will show no trace of crystallisation under the microscope.

L. DE K.

**Reaction of Carbonic Oxide.** By ACHILLE E. MERMET (*Compt. rend.*, 1897, **124**, 621—624).—Carbonic oxide reduces a dilute solution of potassium permanganate acidified with nitric acid, and the change is more rapid in presence of silver nitrate. Precautions are necessary to prevent reduction by organic matter contained in the air or in water. Solutions are prepared as follows. *Silver nitrate*, 2 to 3 grams, in 1000 c.c. of water. *Potassium permanganate*: 1000 c.c. of water is boiled for some time with a few drops of nitric acid free from hydrochloric acid, and permanganate solution is added until a rose-colour is persistent. After cooling, 1 gram of permanganate is dissolved in the water, and 50 c.c. of pure nitric acid added, the solution being kept out of contact with dust and away from the light. The test solution is prepared, just before use, by mixing 20 c.c. of silver nitrate solution with 1 c.c. of permanganate solution, adding 1 c.c. of pure nitric acid, and diluting to 50 c.c. with water free from organic matter.

Two flasks with glass stoppers are filled with water free from organic matter, and one is emptied in presence of the air to be tested, and the other in presence of pure air; 25 c.c. of the reagent is poured into each flask, and they are allowed to stand side by side, with as little exposure to light as possible, and the time necessary for the decolorisation of the permanganate solution is observed. With air containing from 1 part of carbonic oxide in 500 to 2 parts in 10,000, the time required for decolorisation varies from 1 to 24 hours. Hydrocarbons and sulphur compounds also reduce the permanganate solution.

The author was unable to detect any carbonic oxide in the gases liberated by plants in active growth. He suggests that the carbonic oxide that is undoubtedly sent into the air in somewhat large quantities is oxidised to oxalic acid.

C. H. B.

**Modified Method for the Qualitative Analysis of a Mixture of Bases.** By L. LAFAY (*J. Pharm.*, 1897, [vi], 5, 224—228).—The author suggests a method for the detection of the metals not precipitated by hydrogen chloride and hydrogen sulphide. The method does not, however, differ greatly from some of those already in use.

M. W. T.

**Detection and Estimation of Small Quantities of Magnesia in Lime-stones.** By ALEXANDER HERRFELD and A. FÖRSTER (*Chem. Centr.*, 1896, i, 1283; from *Zeit. Ver. Rübenzuck.-Ind.*, 1896, 284—288). —To make a qualitative test, 0·5 gram of the sample is dissolved in 10 c.c. of water with the aid of hydrochloric acid; any iron is oxidised by means of a little nitric acid and then precipitated by boiling with a small excess of calcium carbonate. After filtering, an excess of limewater is added which precipitates any magnesia present.

After decantation and slightly washing the precipitate, it may be

redissolved in hydrochloric acid, freed from lime by means of ammonia and ammonium oxalate, and precipitated with sodium phosphate. It is then, as usual, weighed as pyrophosphate. L. DE K.

**Estimation of Lead in Minerals.** By GIOVANNI GIORGIS (*Gazzetta*, 1896, **26**, 522—527).—The author finds that the following method of estimating lead in galena gives good results. About 2 grams of the powdered mineral is treated with nitric acid, the latter displaced by heating on the water bath with sulphuric acid, and the precipitate, if desired, freed from sulphuric acid by washing by decantation, although this is unnecessary. The product is treated with soda or potash, the solution acidified with acetic acid, to the whole or an aliquot part of the solution excess of standard potassium dichromate solution is added, and the liquid made up to a known volume; the excess of dichromate is determined in an aliquot part filtered from the lead chromate, by reducing with sulphurous anhydride, precipitating with soda, filtering and dissolving the precipitate in sulphuric acid, the latter solution being made up to standard volume, and the chromium determined by titration with permanganate by the author's method (Abstr., 1893, ii, 554). The excess of potassium dichromate added to the lead solution is thus known, and when subtracted from the total quantity added gives the quantity which reacted with the lead, so that the percentage of the latter in the mineral can be calculated.

W. J. P.

**Quantitative Analysis of Refined Copper.** By ERNST MURMANN (*Monatsh.*, 1896, **17**, 697—731).—Wegscheider, in his study of the estimation of copper as cuprous sulphide (Abstr., 1894, ii, 31), having stated that even with careful manipulation an error of 0·3 per cent. might occur, the author has reinvestigated this subject, and finds that cuprous sulphide, prepared from pure copper, and repeatedly heated in hydrogen with the addition of a fragment of sulphur, varies less than $\pm 0·05$ per cent. from the theoretical yield. The safest method of heating is to use a large burner, adjust the air until the luminosity just disappears, and place the crucible about 5 cm. from the top of the burner, so that it is completely surrounded by the flame. When a minute trace of hydrogen sulphide is introduced into the hydrogen, by passing the gas through dilute hydrogen sulphide solution, it is both safe and necessary to raise the crucible to a bright red heat. Cupric sulphide prepared in the wet way is far from pure. Calcium and silica from the vessels are always present, the former only in negligible quantity, but silica in sufficient amount to render it essential that the weighed cuprous sulphide should be dissolved and the insoluble matters collected. The largest error, however, is caused by the presence of alkalis, especially when an alkali sulphide has been used to extract antimony, &c.; they can only be removed by washing the precipitate with hydrogen sulphide solution after ignition. In spite of these defects, the estimation of copper as sulphide is the most accurate method available. Silver and lead must first be removed by adding a few drops of hydrochloric acid to the nitric acid solution and then evaporating with a small excess of sulphuric acid. The filtered solution is then precipitated by hydrogen sulphide as usual. The amounts of

gold, tin, bismuth, antimony, and arsenic in refined copper are usually so small that they need not be separated, since they fall within the limits of the error in the copper estimation itself. The electrolytic method is less exact, owing to the tendency of the reduced copper to absorb moisture from the air even in the desiccator. For the estimation of iron and nickel, it is better to precipitate the bulk of the copper as thiocyanate than as sulphide, since the sulphide always carries down small quantities of those metals. In estimating the lead, enough hydrogen sulphide should be added to the copper solution to throw down only a few centigrams of sulphide. This precipitate will contain all the lead, together with some antimony and bismuth. The lead in it should be estimated electrolytically. Antimony and arsenic are best estimated by heating 50—100 grams of the metal to bright redness for 2 hours in a current of hydrogen. The volatile metals are completely expelled, and are condensed partly in the tube, partly (together with the sulphur) in a hydrochloric acid bromine solution ; lead passes over at the same time, and must be separated by sodium sulphide. If the antimony is weighed as tetroxide, it must afterwards be purified from alkali salts by washing with cold water. Estimation as trisulphide by heating in carbonic anhydride in a Gooch crucible is inexact, since oxygen enters the crucible by diffusion and partially converts the sulphide into oxides. These can, however, be reconverted into sulphide by heating in hydrogen sulphide. The published instructions for the estimation of oxygen in copper require revision. When filings are taken for heating in hydrogen, it is impossible to clean them without incurring superficial oxidation to an extent which may more than double the amount of oxygen. Since filings also are apt to adhere to the glass of the bulb tube during ignition, the weighing of the tube is involved, but as glass cannot be ignited for long without loss of weight, an error is incurred. The copper is best used in the form of rods 4—6 millimetres in diameter and 10—20 mm. long. These are cleansed from grease by benzene or chloroform, and either filed bright or rubbed with dry sand in a bag and wiped, but not dried by heat. They are best heated in a boat placed in a plain tube. The heat must be continued until the weight becomes constant, which may require several hours. The estimation of the cuprous oxide by treatment with silver nitrate yields very fallacious results, the amount of oxygen found being greater than the total ascertained by ignition in hydrogen.

An analysis of Mansfeld copper conducted according to the above principles gave the following results per cent. :

| Cu. | Ag. | Pb. | Fe. | Ni. | Co. | Sb. and As. | S. | O. |
|---|---|---|---|---|---|---|---|---|
| 99·85 | 0·015 | 0·0006 | 0·0057 | 0·0012 | 0·0006 | 0·0002 | 0·0014 | 0·06 |

and metals in the insoluble residue 0·0007, a far greater degree of purity than has been shown by former analyses. M. J. S.

**Estimation of Copper.** By RUDOLF WEGSCHEIDER (*Monatsh.*, 1897, **18**, 44—47).—Attention is called to some misconceptions displayed by Murmann (preceding abstract) in his allusions to a paper of the author's (Abstr., 1894, ii, 31). C. F. B.

**Acetylene as a Quantitative Reagent.** By HENRIK G. SÖDERBAUM (*Ber.*, 1897, **30**, 902—904).—As already stated (this vol., i, 309), on passing acetylene into an ammoniacal solution of a cupric salt, the metal is completely precipitated as black copper acetylide; this precipitation is quantitative, and can be used as a method for the estimation of copper.

Since other metallic solutions are not affected by acetylene, this method can also be employed as a means of separating copper from mixtures containing it; an experiment conducted on a solution containing copper and zinc, showed that no trace of the latter was carried down by the acetylide. J. F. T.

**Analysis of Copper Salts.** By LIVIO SOSTEGNI (*Staz. Sper. Agrar.*, 1895, **28**, 167—180).—The following method is recommended for analysing commercial copper sulphate. The salt (1 gram) is dissolved in water (25 c.c.) in a small Erlenmeyer flask, and the solution treated with 15 c.c. of a solution of Rochelle salt and sodium hydroxide (in the same proportions as used in Fehling's solution); after adding 25 c.c. more water, it is gradually treated with sugar solution, and boiled for 5 minutes. Freshly boiled water (25 c.c.) is added, the liquid allowed to subside a little, and filtered through a filter free from ash; with a good filter, the cuprous oxide can be washed free from alkali in 5 to 10 minutes. The dried oxide is then put into a platinum boat, together with the burnt filter, and reduced in a current of hydrogen. The copper can be readily removed from the platinum boat; although occasionally a little nitric acid has to be used to dissolve the last traces. The method is quick, and gives very good results. Small quantities of iron do not affect the result. If, however, more iron is present, the solution is heated with a slight excess of ammonia, filtered and boiled; the analysis is then continued as described.

*Estimation as Cuprous Sulphide.*—The copper is precipitated as cupric sulphide in the manner described by Fresenius (*Quant. Anal.*, vol. I), filtered, and quickly dried. The filter with the precipitate is then burnt on a platinum wire, dropped into a porcelain boat, covered with a little finely powdered sulphur, and heated in a current of hydrogen. The method gives very good results, equal to those obtained by the electrolytic method.

The first method may also be employed for estimating sugar in must and wines, &c. The must (5 c.c.), in a 100 c.c. flask, is treated with basic lead acetate solution (4 c.c.) and 20 per cent. sodium carbonate (4 c.c.), diluted to 100 c.c., and a portion filtered through a dry filter. Of the filtrate, 10 c.c. is treated with 25 c.c. of Fehling's solution diluted with four times its bulk of water, boiled for 2 or 3 minutes, and allowed to cool; the supernatant liquid is poured off through a filter, and the precipitate washed with hot water. The analysis is then continued as described. As regards the relation of the amount of copper to sugar, with solutions containing not more than 0·5 per cent. of sugar, 50 milligrams of sugar seems to correspond with about 96·0 of copper (Meissl), whilst with 0·5—1·5 per cent. solutions, the same amount of sugar corresponds with about 93·7 of copper (Herzfeld). N. H. J. M.

**Quantitative Analysis with Aid of Hydrazine Sulphate.** By ATTILIO PURGOTTI (*Gazzetta*, 1896, **26**, ii, 559—573).—Hydrazine sulphate may be advantageously used in the estimation of copper, chromic acid, and manganese dioxide, inasmuch as it reduces these substances, giving a quantitative yield of nitrogen.

On boiling copper sulphate solution with sodium chloride and hydrazine sulphate, reaction occurs in accordance with the equation $4CuSO_4 + 10NaCl + N_2H_4,H_2SO_4 = 2Cu_2Cl_2 + 5Na_2SO_4 + 6HCl + N_2$; this reaction is applied to the estimation of copper sulphate in the following way. The aqueous solution of the cupric salt containing excess of sodium chloride is boiled to expel air, in a suitable apparatus, and a slight excess of a well-boiled concentrated solution of hydrazine sulphate introduced; the mixture is then boiled until colourless, the nitrogen collected in a eudiometer, and its volume at N. T. P. ascertained in the usual way. 100 c.c. of nitrogen at N. T. P. is equivalent to 1·1313 gram of copper.

Potassium dichromate reacts with hydrazine sulphate in sulphuric acid solution in accordance with the equation $2K_2Cr_2O_7 + 5H_2SO_4 + 3N_2H_4,H_2SO_4 = 2Cr_2(SO_4)_3 + 2K_2SO_4 + 3N_2$; so that 100 c.c. of nitrogen at N. T. P. is equivalent to 0·87577 gram of potassium dichromate, or 0·59576 gram of chromic anhydride; the determination is carried out just as with cupric salts, but no sodium chloride is used and the hydrazine solution is acidified with sulphuric acid.

Manganese dioxide readily reacts with hydrazine sulphate in acid solution in accordance with the equation $2MnO_2 + H_2SO_4 + N_2H_4,H_2SO_4 = 2MnSO_4 + 4H_2O + N_2$, and in neutral solutions a similar reaction occurs, but hydrazine hydrate is formed; 0·77861 gram of manganese dioxide liberates 100 c.c. of gas at N. T. P. The determination may be performed in acid or neutral solutions, either hot or cold, but if ferric oxide is present it reacts with the hydrazine sulphate in hot acid solution, although not in neutral or in cold acid solutions.

The test analyses gave good results. W. J. P.

**Separation of Thorium from the other Rare Earths by means of Potassium Trinitride [Azoimide].** By LOUIS MUNROE DENNIS (*J. Amer. Chem. Soc.*, 1896, **18**, 947—952).—The author has proved by a large number of experiments that thorium may be quantitatively separated from cerium, lanthanium, and didymium by boiling the neutralised solution with a solution of potassium azoimide. The thorium is precipitated as hydroxide, a corresponding amount of azoimide escaping.

The reagent is prepared by nearly neutralising a dilute solution of azoimide with aqueous potash. L. DE K.

**Estimation of Thoria and its Behaviour with Oxalic Acid and Ammonium Oxalate.** By CHARLES GLASER (*Zeit. anal. Chem.*, 1897, **36**, 213—219).—The author admits the correctness of Hintz and Weber's statement (this vol., ii, 162) that a thoria solution, mixed with a large excess of ammonium oxalate, gives no precipitate even on cooling. The presence of ammonium acetate increases the solubility. Excess of hydrochloric acid completely precipitates the thorium from these solutions, seemingly as the salt $ThH_2(C_2O_4)_3 + 2H_2O$. Zirconium

oxalate is soluble in hydrochloric acid. A separation of thorium from the zirconium oxides by ammonium oxalate is complete only when a larger excess of the oxalate than just suffices for dissolving the zirconium oxalate is avoided. Cerium oxalate is somewhat soluble in ammonium acetate, and the use of a large amount of this salt must therefore be avoided when separating thorium and cerium. M. J. S.

**Estimation of Manganese in Cast Iron.** By FERDINAND ULZER and JULIUS BRÜLL (*Chem. Centr.*, 1896, i, 769; from *Mitt. techn. Gew. Mus. Wien*, 1895, 312).—The liquid, after being freed from iron by means of zinc oxide according to Volhard's directions, is mixed with 20 c.c. of a 5 per cent. solution of hydrogen peroxide. Aqueous soda is added as long as a precipitate forms, and the mixture is boiled. When cold, standard solution of oxalic acid is added, and then dilute nitric acid, the mixture is heated nearly to boiling, and the excess of oxalic acid in the clear solution is titrated with standard permanganate solution.

The best solvent for the iron is a mixture of 10 vols. of nitric with 2 vols. of sulphuric acid and 10 vols. of water; during the evaporation of the solution, 10 c.c. of hydrochloric acid is added. The liquid should contain about 0·1 gram of manganese. L. DE K.

**Estimation of Manganese and Chromium in Products of the Iron Industry.** By GIOVANNI GIORGIS (*Gazzetta*, 1896, **26**, ii, 528—536).—The author modifies Volhard's process (Abstr., 1880, 141) for determining manganese as follows. The solution of the blast furnace or other product containing iron and manganese is treated with sodium carbonate until a slight precipitate forms, which is then dissolved by nitric acid free from nitrous acid, and the solution diluted to standard volume. A known volume of N/20 potassium permanganate, more than sufficient to oxidise all the manganese present, is boiled for some time in a basin with a large quantity of sodium nitrate and an aliquot part of the manganese and iron solution; after cooling and diluting to a standard volume, an aliquot part of the solution is separated through an asbestos filter and the excess of permanganate titrated with N/20 chromium sulphate solution. From the excess of permanganate thus ascertained, the quantity of manganese in the original solution can be calculated.

This method is not directly available for the estimation of chromium; if chromium but not manganese be present, the former can be determined by substituting for the sodium nitrate added to the boiling permanganate solution, a solution containing 40 grams of potassium carbonate and 0·5 gram of potash per litre; this is added to the permanganate solution which is then boiled with the chromium solution for a short time, after the latter has been neutralised with sodium carbonate. The excess of permanganate used is determined as before.

If the solution contains iron, manganese, and chromium together, it is treated with sodium carbonate, clarified with nitric acid, and boiled for some time with excess of permanganate containing much sodium nitrate; the liquid is then rendered alkaline by adding the above solution of potassium carbonate and potash, and after again boiling is

made up to a standard volume, an aliquot part filtered off through an asbestos filter, and the excess of permanganate used determined as before. The quantity of permanganate requisite to oxidise both chromium and manganese is thus ascertained, and by determining one of these metals by either of the methods described above, the quantity of each present can be found.

The test analyses gave good results. W. J. P.

**Estimation of Tungsten in Ferro-Tungstates.** By HEINRICH WDOWISZEWSKI (*Chem. Centr.*, 1896, i, 770; from *Przeglad. Techniczny*, 1896, Zeszyt, I).—About 1 gram of the sample is fused with 6 times its weight of a mixture of 2 parts of dry borax and 3 parts of potassium sodium carbonate; the fused mass on being exhausted with boiling water leaves the ferric oxide undissolved. The filtrate is mixed with excess of hydrochloric acid, evaporated to dryness, and the residue treated with dilute hydrochloric acid, which leaves the tungstic and silicic acids undissolved. The tungstic acid is then dissolved in ammonia, and reprecipitated by adding hydrochloric acid.

L. DE K.

**Estimation of Antimony as Tetroxide.** By HENRI BAUBIGNY (*Compt. rend.*, 1897, **124**, 499—502).—The existing statements as to the stability of antimony tetroxide at high temperatures are conflicting, and the author has made experiments with a view to ascertain whether antimony can be accurately estimated in the form of this oxide. Pure antimonic acid prepared from the pentachloride by the action of water, and dried at 100°, was heated in porcelain dishes, in a glass or porcelain tube, at 357°, 440°, 550—600°, and 800°. At 357°, the weight becomes practically constant after heating for many hours, and the product seems to be antimonic anhydride. At 440°, decomposition begins and continues as the temperature is raised to 800°, but after 2 hours at the latter temperature the weight of the oxide becomes constant, and it has the composition $Sb_2O_4$. No further change takes place if the oxide is maintained at 800° for several hours, and it follows that the tetroxide is stable at this temperature. It begins to decompose, however, if the temperature is raised to the melting point of silver. C. H. B.

**Estimation of Paraffin in the Last Fractions of Brown-Coal Tar and Crude Petroleum.** By D. HOLDE (*Zeit. angw. Chem.*, 1897, 116—117).—The author dissolves the sample in the smallest possible amount of ether and precipitates the paraffin by adding the smallest excess of absolute alcohol. The temperature should be as low as $-18$ or $-21°$. The paraffin is washed on a weighed filter with a mixture of alcohol and ether of the same temperature.

L. DE K.

**Detection of the Adulteration of Essential Oils.** By ÉMILE GOSSART (*Bull. Soc. Chim.*, 1896, [iii], **15**, 597—609).—When a mixture of liquids is added drop by drop, with certain precautions, to another liquid mixture, containing the same constituents, the former will not merge at once in the latter, but will assume a spheroidal state when the composition of the two liquids is nearly the same (compare

Abstr., 1892, 236). When, however, the composition of the one differs from that of the other by more than a certain amount, the two liquids mix at once and will not exhibit the above phenomenon. Upon this fact, the author has based a method, to which he gives the name of *homeotropy*, for the detection of the adulteration of certain essential oils. In this method, the suspected oil is allowed to drop from a pipette into a specially constructed glass dish containing some of the essential oil of known purity, when, if pure, it will exhibit the spheroidal phenomenon above described. It is found, for example, that this phenomenon is only manifested by mixtures of oil of bitter almonds and alcohol, when these differ in composition by less than 2 per cent. whenever oil of bitter almonds contains more than 3 per cent. of alcohol, a drop of the mixture invariably merges at once in the pure oil when added in the manner described by the author. In the case of mixtures of oil of bitter almonds and nitrobenzene, it is necessary, on account of the high viscocity of the liquid, to dilute with alcohol when applying this method. Estimations of any given adulterant may be made by adding to the genuine essential oil such measured quantities of the adulterant in question as will give rise to the spheroidal phenomenon with the impure liquid. A. C. C.

**Detection of the Adulteration of Essential Oils.** By ÉMILE GOSSART (*Bull. Soc. Chim.*, 1897, [iii], **15**, 666—688, 724—741).—An account of the composition and proportion of the commoner essential oils, of the substances with which they are usually adulterated, and of the application of the author's method (preceding abstract) for detecting or estimating the adulteration. M. W. T.

**Volumetric Estimation of Ethylic Alcohol and Ethylic Acetate in Admixture.** By BASIL B. KURILOFF (*Ber.*, 1897, **30**, 741—743).—Ethylic alcohol and ethylic acetate are quantitatively converted into acetic acid when they are heated at 100° for 4—6 hours with an acid solution of potassium dichromate, and this method can readily be used for their estimation. The oxidation is effected by means of potassium dichromate (1 gram in 100 c.c.) and dilute sulphuric acid, the excess of chromic acid after the reaction has been completed being determined by means of potassium iodide and sodium thiosulphate. The error in the estimation of 0·1—0·15 gram of either substance is less that 0·5 per cent. To analyse a mixture of acetic acid, ethylic acetate, and ethylic alcohol, three processes are necessary. 1. Titration of the acetic acid. 2. Hydrolysis of the ethylic acetate with excess of baryta water and titration of the excess with sulphuric acid. 3. Oxidation of the total ethylic acetate and ethylic alcohol by potassium dichromate. A. H.

**Estimation of Glycerol in Wine and the Indirect Estimation of Mannitol in Mannitic Wines.** By G. MANCUSO-LIMA and GIUSEPPE SGARLATA (*Staz. Sper. Agrar.*, 1895, **28**, 236—245).—The wine (25 c.c.) is evaporated to a very small volume in a porcelain dish on a water bath, treated with a slight excess of basic lead acetate and excess of ammonia, and quickly filtered; the precipitate is washed two or three times, the funnel being covered with a larger funnel, the tube of which is connected with a flask containing caustic potash (to avoid

possible decomposition of the lead glucosate by carbonic anhydride during the filtration). The filtrate is collected in a beaker, supersaturated with pure, concentrated sulphuric acid, again filtered, boiled, and permanganate run in until the liquid becomes red, the boiling being maintained. The number of c.c. of permanganate added multiplied by 0·01 gives the amount of glycerol in the 25 c.c. of wine.

*Indirect Estimation of Glycerol.*—Fifty c.c. of wine is evaporated down, treated with a slight excess of basic lead acetate, filtered, washed, and diluted to 500 c.c. Of this, 250 c.c. is treated with sodium carbonate, filtered, made up to a definite volume and the glucose determined with Fehling's solution. The other 250 c.c. of the solution is saturated with sulphuric acid, filtered, washed, and the boiling solution oxidised with normal permanganate solution. The amount of permanganate required to oxidise the glucose, as determined, is calculated and deducted from the amount actually used. The number thus obtained multiplied by 0·01 gives the amount of glycerol in 25 c.c. of wine.

*Indirect Estimation of Mannitol.*—The glycerol is determined by the direct method first described. Another 50 c.c. of the wine is treated exactly as for the indirect estimation of glycerol. The number of c.c. of permanganate *minus* the amount corresponding with the glucose and glycerol, multiplied by 0·0089 gives the amount of mannitol in 25 c.c. of wine.
N. H. J. M.

**Estimation of Pentoses and Pentosans by Means of the Furfuraldehyde Distillation.** By MARTIN KRÜGER and BERNHARD TOLLENS (*Chem. Centr.*, 1896, 1, 576—577; from *Zeit. Ver. Rübenzuck.-Ind.*, 1896, 21—25).—From 2 to 5 grams of the fodder is distilled with 100 c.c. of 12 per cent. hydrochloric acid until 30 c.c. has passed over, another 30 c.c. of acid is then added, and the operation repeated until the distillate no longer reddens paper saturated with a solution of aniline acetate. A solution of phloroglucinol in dilute hydrochloric acid is now added to the distillate, and the whole is made up with acid to 400 c.c. and allowed to remain overnight. The precipitate is then collected on a weighed filter, washed, dried at 97°, and weighed. To calculate the amount of furfuraldehyde, the weight of the precipitate is divided by 1·82 if it does not exceed 0·2 gram; by 1·93 if it amounts to 0·5 gram, and by corresponding factors if it comes between the two.

To calculate the furfuraldehyde into the respective pentosans and pentoses, 0·0104 is first deducted and the difference is multiplied by the following factors: 1·68 for xylan, 2·07 for araban, or 1·88 for pentosans in general, 1·91 for xylose, 2·35 for arabinose, or 2·31 for the pentoses in general.
L. DE K.

**Electrolytic Estimation of Copper in Sugar Analysis.** By G. TARULLI (*Gazzetta*, 1896, **26**, ii, 485—495).—In order to ascertain whether, in the reduction of Fehling's solution by sugars, the copper may be advantageously estimated electrolytically, the author, after titrating the sugar solution with standard Fehling, determines the copper remaining in solution by weighing it as electrolytically deposited metal, and then dissolves the cuprous oxide which has been filtered off in nitric acid, displaces the latter by sulphuric acid, and after electro-

lysing, weighs the copper originally precipitated, as oxide; the comparison of the quantity of copper in the Fehling solution used with the sum of the two quantities of copper thus deposited electrolytically shows that the process is accurate. Copper may be deposited electrolytically from alkaline Fehling solution and weighed as metal with nearly the same accuracy as from acid solutions. The cuprous oxide is best filtered off through Berzelius filter paper, and Missaghi's suggestion that a piece of glass rod should be placed between the filter and funnel to expedite filtration should be adopted; the oxide is prevented from creeping over the edge of the filter by turning the latter in several millimetres below the top. Instead of converting the cuprous oxide into nitrate and then into sulphate, satisfactory results may be obtained by electrolysing the solution of the oxide in a mixture of 3 parts of nitric acid (sp. gr. = 1·18) and 8 parts of sulphuric acid (sp. gr. = 1·07).

The author finds that, taking Cu = 63·34, inverted cane-sugar reduces 9·77 equivalents of cuprous oxide. W. J. P.

**Reducing Powers of Various Sugars Determined by the Electrolytic Process.** By G. TARULLI and E. MAMELI-CUBEDDU (*Gazzetta*, 1896, **26**, ii, 495—502).—The authors have determined the reducing powers of various sugars by Tarulli's process (see preceding abstract), using normal and one-fourth normal Fehling's solution. The reducing powers obtained by them and by Soxhlet are given in the following table:

| | Tarulli and Cubeddu. | | Soxhlet. | |
|---|---|---|---|---|
| | Normal. | Dilute. | Normal. | Dilute. |
| Dextrose | 10·748 | 10·632 | 10·52 | 10·11 |
| Lactose | 7·238 | 8·559 | 7·4 | 7·4 |
| Galactose | 10·003 | 10·187 | 9·8 | 9·4 |
| Maltose | 8·682 | 8·02 | 6·9 | — |

The observation of Soxhlet and Brumme, namely, that the first portions of dextrose added to Fehling's solution are more completely reduced than the later ones, is confirmed, the authors finding that the cupric-reducing power of the glucose gradually diminishes as its addition proceeds. W. J. P.

**Estimation of Sugar in Animal Liquids.** By E. RIEGLER (*Zeit. anal. Chem.*, 1897, **36**, 280; from *Wiener med. Blätt.*, 1896, 451).—Fehling's solution is reduced by an excess of phenylhydrazine with evolution of nitrogen. The difference between the volume of nitrogen obtained from 5 c.c. of Fehling's solution and the same after partial reduction by the sugar to be estimated is reduced to grams and multiplied by 2·6. M. J. S.

**Estimation of Sugar in Urine.** By AUGUSTA JASSOY (*Chem. Centr.*, 1896, i, 578—579; from *Apoth. Zeit.*, ii, 34—35).—The urine,

which, if alkaline, should be acidified with tartaric acid, is fermented in a special apparatus with yeast, and the carbonic anhydride produced is found by noticing the volume of air before and after absorption by aqueous potash.

It is difficult to see in what respect this process is preferable to those ordinarily used, as nothing like the theoretical amount of carbonic anhydride has been obtained by the author. L. DE K.

**Estimation of the Caramel on the Surface of Coffee Berries Roasted with Sugar.** By WILHELM FRESENIUS and LEO GRÜNHUT (*Zeit. anal. Chem.*, 1897, **36**, 225—233).—Four methods have been proposed for this purpose, namely, those of Neubauer, König, Stutzer, and Hilger. Stutzer's is the one favoured by the Conference of Bavarian Technical Chemists, but the authors, after testing the four methods side by side, give the preference to Hilger's. Neubauer's and König's processes depend on the extraction of the berries with hot water, and the results are unquestionably too high. In Stutzer's process, 10 grams of the unground coffee is shaken for 5 minutes with 250 c.c. of cold water, made up to 500 c.c., the extract decanted immediately, filtered, and its solid contents (drying at 100°) and ash ascertained.

Experiments with coffee to which no sugar had been added show that an appreciable portion of the extractive matter consists of normal coffee constituents, and if these are deducted the results are too low. In Hilger's process, 10 grams of whole coffee is digested three times, for half an hour each time, with 100 c.c. of a mixture of equal volumes of water and 90 per cent. alcohol at atmospheric temperature. Each portion of extract is decanted, and the united extracts are made up to 500 c.c., filtered, and residue and ash ascertained as before. If from the numbers thus obtained there is deducted a constant (1·07 of dry residue, or 0·83 of ash-free residue per 100 parts of dry coffee), which is the average of four experiments on genuine coffee roasted until it has undergone a normal loss of 18 per cent., the remainder may be regarded as representing the caramel present, and agrees approximately with the numbers obtained in Stutzer's method without any deduction.

M. J. S.

**Estimation of Alcapton (Homogentisic Acid) in Urine.** By GEORGES DENIGÈS (*J. Pharm.*, 1897, [vi], **5**, 50—54).—See this vol., ii, 337.

**Estimation of Filicic Acid in Officinal Preparations of the Male Fern.** By GIROLAMO DACCOMO and L. SCOCCIANTI (*J. Pharm.*, 1897, [vi], **5**, 61—62).—The aqueous solution of filicic acid, or the rhizome of the fern itself, is extricated with ether and the ethereal extract agitated with a solution of copper acetate. The copper filicate is collected, washed with water and alcohol, dried at 100°, and weighed. Pure ether should be used for the extraction, as the presence of a small quantity of alcohol lowers the solubility of the filicic acid considerably. M. W. T.

**Qualitative Examination of Butter.** By EMIL JAHR (*Chem. Centr.*, 1896, i, 462; from *Milch. Zeit.*, **24**, 766—767).—The melted

fat is shaken in a test-tube with twice its volume of water at 31°, and the tube is then placed in water at 50°. Margarine readily separates whilst butter remains emulsified for some time. In a mixture of margarine and butter, two distinct layers will be visible.

On adding sulphuric acid, then hydrochloric acid, and finally a little permanganate solution, the margarine retains its yellow colour, and readily separates from the aqueous layer, whereas butter is completely bleached, and separates with difficulty; a mixture of the two will remain more or less yellow, and will partly stick to the sides of the test-tube. If brine is used instead of water, the margarine separates as a clear yellow layer covered at the top and bottom with a flocculent, opaque mass. If as little as 10 per cent. of butter is present, the fat separates as a homogeneous, opaque, dirty yellow mass.

L. DE K.

**Detection of Margarine in Cheese.** By VON RAUMER (*Zeit. angw. Chem.*, 1897, 77—82).—The author has not obtained satisfactory results by extracting the fat with ether and submitting it to the usual tests, as the fat in cheese is always sensibly decomposed.

Better results are obtained by rubbing cheese with water, and adding a solution of copper sulphate, which causes the formation of a dense precipitate containing the fat, whilst the free fatty acids remain in the mother liquor; the precipitate is finally extracted with light petroleum of low boiling point. L. DE K.

**Estimation of Tannin in Wine.** By AGOSTINO VIGNA (*Staz. Sper. Agrar.*, 1895, **28**, 19—22. Compare Abstr., 1891, 1399).—Instead of zinc acetate, potash alum may be employed for precipitating the tannin. The process is as follows: 8 per cent. alum solution (40 c.c.) is added to the wine (50 c.c.), and the acid exactly neutralised with ammonia. The mixture is shaken, filtered through a plain filter, the precipitate washed with cold water, and finally washed out into the original dish. It is then dissolved in dilute sulphuric acid (1 : 4) and titrated in the cold with permanganate after addition of a known amount of indigo solution.

The method gives results agreeing with those obtained by the ammoniacal zinc acetate method. N. H. J. M.

**Detection of "Saccharin" in Beer.** By WAUTERS (*Chem. Centr.*, 1896, i, 576; from *Mon. scient.*, [iv], **10**, 146—147).—Beer containing "saccharin" usually has a low density, and also contains but little solid matter. The author rejects as untrustworthy the tests for "saccharin" based on the detection of its sulphur; the reaction with resorcinol and sulphuric acid is utterly condemned. He considers the best test to be the one based on the formation of salicylic acid, when "saccharin" is gently fused with potassium hydroxide. L. DE K.

**Urometer for Small Quantities of Urine.** By ADOLF JOLLES (*Zeit. anal. Chem.*, 1897, **36**, 221—223).—A miniature hydrometer (103 mm. in length) with a scale ranging from sp. gr. 1·000 to 1·010, but furnished with weights by which readings up to 1·050 can be obtained with the use of 20 c.c. of liquid. M. J. S.

# General and Physical Chemistry.

**Molecular Dissymmetry and the Rotatory Power of Active Homologous Compounds.** By PHILIPPE A. GUYE and L. CHAVANNE (*Bull. Soc. Chim.*, 1896, [iii], 15, 177—195 and 275—305).—The authors give a detailed account of the preparation of the various optically active compounds which they have examined (compare Abstr., 1895, i, 202 and 317). The study of these compounds, and of a number of others prepared and examined by different observers, leads to the following generalisations.

1. For any substance containing one asymmetric carbon atom, C *a b c d*, in which the heaviest group alone is allowed to vary, the formula for the product of asymmetry indicates that the rotatory power reaches a maximum, and that the values then decrease; if the heaviest group, *a*, is already large as compared with the other three, the rotatory powers may decrease continually from the first term.

2. In the 23 series of homologous compounds examined, 16 show values of $[\alpha]_D$ which reach a maximum, whilst in the case of the remaining 7 the values of $[\alpha]_D$ decrease regularly with rising molecular weight.

3. In a number of instances, the observed maximum of $[\alpha]_D$ does not coincide with the calculated maximum value of $P$, although the maximum of $P$ is usually very close to that of $[\alpha]_D$.

4. These results only hold when the compounds are strictly homologous. If, for example, in any series of normal compounds the butylic is replaced by the isobutylic radicle, or an atom of chlorine by an atom of bromine, the regularity is destroyed.

5. Isomeric compounds may therefore have very different rotatory powers, and the rotatory power depends, not merely on the masses of the groups, but on their relative positions one to another. H. C.

**Measurement of the Capacity of Polarisation.** By C. M. GORDON (*Ann. Phys. Chem.*, 1897, [ii], 61, 1—29).—For small currents, polarisation is a reversible process, and if $E$ is the force which it sets up, $c$ the capacity, $j$ the current, and $t$ the time, the Kohlrausch formula $E = 1/c\int jdt$ holds; if, however, the current is increased beyond a certain value, the capacity does not remain constant, and the formula no longer applies. When mercury electrodes are used, the capacity depends primarily on the number of dissolved mercury ions in the solution. The capacity in the case of platinum electrodes depends both on the quantity of occluded hydrogen or oxygen and on the concentration of the electrolytes. Resistances can be accurately determined with platinised platinum electrodes, but the values obtained are too great when the electrodes are not platinised. H. C.

**Determination of the Dielectricity Constants of some Salt Solutions by the Electrometric Method.** By FREDERIC J. SMALE (*Ann. Phys. Chem.*, 1897, [ii], 61, 625—628).—The dielectricity con-

stants of the following salt solutions were determined, and are given in terms of water as unity :

| Normal conc. | KCl. | HCl. | $CuSO_4$. | Mannitoboric acid. |
|---|---|---|---|---|
| 0·001 | 1·013 | 0·990 | — | |
| 0·002 | 1·018 | 1·033 | 1·012 | |
| 0·005 | 1·034 | 1·064 | 1·017 | |
| 0·008 | 1·070 | 1·090 | 1·050 | |
| 0·010 | 1·113 | 1·126 | 1·086 | |
| 0·030 | 1·160 | | | |
| 0·020 | | | 1·128 | |
| 0·050 | | | 1·155 | |
| 0·333 | | | | 1·007 |
| 0·666 | | | | 1·019 |

It is especially noteworthy that the solutions have greater dielectricity constants than pure water, but no explanation of this fact can yet be given. The dielectricity constants are not proportional to the conductivities. H. C.

**Electrical Conductivity of Nitramide.** By E. BAUR (*Annalen*, 1897, **296**, 95—100. Compare this vol., ii, 25).—The electrical conductivity of nitramide at 0° is stated by Hantzsch and Kaufmann (*loc. cit.*) to be $\mu_{32} = 1{\cdot}95$, and $\mu_{63} = 1{\cdot}69$ ; a decrease of conductivity accompanying dilution is inconsistent with the dissociation hypothesis, and the author has therefore performed a series of observations with a specimen of nitramide obtained from nitrourethane, and several times recrystallised. The values obtained are in opposition to the result of the above-mentioned investigators, the electrical conductivity increasing with dilution, and when $v = 63{\cdot}105$, the conductivity, $\mu = 1{\cdot}126$ ; the higher value recorded by Hantzsch and Kaufmann is attributed to the presence of nitric acid in the specimen of nitramide employed.

In considering the isomerism of compounds having the formula $N_2O_2H_2$ (this vol., ii, 26), Hantzsch states that nitramide is 500 times more feebly acidic than acetic acid; the conductivity of acetic acid, however, is observed by the author to be only five or six times greater than that of nitramide, so that if acidity is regarded as nearly proportional to this constant, acetic acid is not more than five or six times more strongly acidic than nitramide. It is, however, approximately true that the dissociation constant of acetic acid is 500 times that of nitramide.

The author is of opinion that the corrected conductivity constant of nitramide differs so considerably from that of hyponitrous acid as to indicate structural isomerism, and not stereoisomerism as advocated by Hantzsch (*loc. cit.*). M. O. F.

**Electromotive Force and Partition Equilibrium.** By ALFRED H. BUCHERER (*Zeit. physikal. Chem.*, 1897, **22**, 590—597).—The author replies to the criticisms of Luther (this vol., ii, 240), and points out that his deductions were purely thermodynamical, inasmuch as they involved no assumption regarding the state of substances in solution, &c., although experimental facts, not involving any hypotheses or

speculation were of course used. The author further adds instances which he holds are not in accord with Nernst's theory, the fundamental fault of which is, in the author's opinion, that it employs fictitious physical constants instead of the actual ones. L. M. J.

**Heat of Formation of Formaldehyde.** By MARCEL DELÉPINE (*Compt. rend.*, 1897, **124**, 816—819).—The action of ammonia on aqueous solutions of formaldehyde develops $+16·6$ Cal. for each molecule of ammonia, and it follows that $6CH_2O$ diss. + $4NH_3$ diss. = $C_6H_{12}N_4$ diss. + $6H_2O$ develops + 66·4 Cal. If the heat of formation of hexamethylene from its elements is taken as $-21·9$ Cal., it follows that $C + H_2 + O = H·CHO$ diss. develops + 40·3 Cal. If $-21·3$ Cal. is taken as the heat of formation of hexamethylene, that of formaldehyde becomes 40·4 Cal. The heat of dissolution was measured by passing hydrogen mixed with formaldehyde vapour into water, and the value obtained is 15 Cal., which is relatively very high. The heat of formation of gaseous formaldehyde must be $+25·4$ Cal. C. H. B.

**Solutions of Trichloracetic Acid.** By PAUL RIVALS (*Compt. rend.*, 1896, **123**, 240—242).—The heat of neutralisation of trichloracetic acid with potassium hydroxide, or with ammonia, varies considerably with the dilution. Thus, a solution of trichloracetic acid containing 1 gram-molecule per litre, when neutralised with a dilute ammonia solution, gave 13·85 Cal., and a solution of the acid containing a gram-molecule in 4 litres gave 13·10 Cal. The difference is mainly due to the heat of dilution of trichloracetic acid, which is found to be very appreciable. The author gives an expression for the heat of solution of solid trichloracetic acid, from which it would appear that the heat of solution in 0·4 litre is zero, that it rises to 2·7 Cal. in 8 litres, and falls to —2·53 Cal. in 0·11 litre. H. C.

**Calorimetric Investigations. Heat of Combustion of the Amides and Anilides of the First Members of the Series of Dibasic Acids.** By FRIEDRICH C. A. STOHMANN and EMIL HAUSSMANN (*J. pr. Chem.*, 1897, [ii], **55**, 263—284. Compare Abstr., 1895, ii, 482).—The heat of combustion of several amic acids, and of their phenylic derivatives, amides, anilides, imides, ammonium salts, and ethereal salts, has been determined. It is found that phenyloxamic (oxanilic) acid and its derivatives yield appreciably higher values than do the isomeric phthalamic acid derivatives; this is connected with the fact that the first acid has a much higher conductivity constant than the second. Unsymmetrical diphenylcarbamide has a slightly larger heat of combustion than the symmetrical compound; as usually happens in such cases, the first is the compound with the lower melting point. The difference between the heats of combustion of succinic acid and its derivatives and those of the corresponding derivatives of malonic acid is less than the normal difference for $CH_2$ (156·6 Cal.), and still smaller is the difference between malonic and oxalic derivatives; connected with this is the fact that the conductivity constant of oxalic acid is much greater than that of malonic, and that of malonic acid than that of succinic. The heats of combustion of diamides are greater than those of the corresponding amic acids, and these than those of the corresponding dibasic acids, by 74·9 Cal. in the mean. Using this

number, the heat of combustion of carbonic acid can be calculated from that of carbamide giving the value +2·4 Cal.. Further, the heat of the changes: dibasic acid + ammonia (liquid) = amic acid + water; amic acid + ammonia (liquid) = diamide + water is in both cases 10·2 Cal. in the mean. The heats of combustion of dianilides are greater than those of the phenylamic acids, and these than those of the dibasic acids, by 804·9 Cal. in the mean; hence the heat of the changes: dibasic acid + aniline = phenylamic acid + water; phenylamic acid + aniline = dianilide + water is in both cases + 5·8 Cal. in the mean. The formation of a diamide or dianilide (and water) from the ammonium or aniline salt of the acid, and also that of an imide (and water) from an amic acid, is accompanied by a slight absorption of heat, except in the case of the phthalic derivatives, where there is a very slight development of heat. The substitution of phenyl for hydrogen in the amido-group increases the heat of combustion by 730·1 Cal. The heat change: dibasic acid + ammonia (liquid) = diammonium salt is 2 × 13·7 Cal.; that of oxalic acid + aniline = aniline oxalate is 2 × 9·65. The heat of the change: amic acid + alcohol = alkylic amate + water is − 1·5 Cal.; using this number, the heat of combustion of phenylcarbamic (carbanilic) acid can be calculated to be 801·1 Cal., and that of carbamic acid itself to be 70·6 Cal. The actual experimental results are given below, in so far as they appear to be new.

| | Heat of combustion. | Heat of formation. | | Heat of combustion. | Heat of formation. |
|---|---|---|---|---|---|
| Oxamic acid | 132·0 | 159·5 | Phthalamide | 921·7 | 106 3 |
| Phenyloxamic acid | 863·1 | 130·4 | Phenylphthalamide | 1651·1 | 78·9 |
| Phenylmalonamic acid | 1013·4 | 143·1 | Diphenylphthalamide | 2383·2 | 48·8 |
| Phenylsuccinamic acid | 1166·5 | 153·0 | | | |
| Phthalamic acid | 850·7 | 142·8 | Succinimide | 438·1 | 110·4 |
| Phenylphthalamic acid | 1577·9 | 117·6 | Phenylsuccinimide | 1168·5 | 82·0 |
| | | | Phthalimide | 850·2 | 74·3 |
| Phenylcarbamide | 880·0 | 54·0 | Phenylphthalimide | 1579·1 | 47·4 |
| Diphenylcarbamide, sym | 1612·8 | 23·2 | | | |
| ,, unsym. | 1614·2 | 21·8 | Ammonium oxalate | 193·8 | 270·2 |
| Tetraphenylcarbamide | 3075·0 | −35·0 | ,, malonate | 349·6 | 277·4 |
| Oxamide | 203·3 | 122·7 | ,, succinate | 502·8 | 287·2 |
| Phenyloxamide | 937·5 | 90·5 | ,, phthalate | 923·0 | 243·0 |
| Oxanilide | 1665·4 | 64·6 | Aniline oxalate | 1662·3 | 205·7 |
| Malonamide | 358·8 | 130·2 | | | |
| Dimethylmalonamide, sym | 686·0 | 129·0 | Ethylic carbamate | 397·5 | 126·0 |
| Diethylmalonamide, sym | 995·1 | 145·9 | ,, phenylcarbamate | 1128·3 | 62·7 |
| Phenylmalonamide, anhydrous | 1088·9 | 102·1 | Methylic oxamate | 304·7 | 149·8 |
| ,, cryst. | 1088·7 | 136·8 | Ethylic oxamate | 457·7 | 159·8 |
| Diphenylmalonamide | 1818·0 | 75·0 | Ethylic phenyloxamate | 1191·2 | 128·3 |
| Succinamide | 509·7 | 142·3 | | | |
| Phenylsuccinamide | 1244·6 | 109·4 | Aniline | 810·7 | −5·2 |
| Succinanilide | 1971·3 | 84·7 | | | |

C. F. B.

**Modification of the Beckmann Apparatus.** By Wilhelm Meyerhoffer (*Zeit. physikal. Chem.*, 1897, 22, 619—625).—The author describes a form of Beckmann apparatus available either for freezing point or solubility determinations, both of which give points on the temperature/concentration curve. A diagram of the apparatus is given and experiments are recorded on the freezing point depression of phenol by thymol at various concentrations. The chief features in the apparatus are (1) the use of a Witt stirrer, with the thermometer in its hollow axis, and (2) a form of "inoculating pencil" whereby, by

the introduction of a minute portion of solidified mass, overcooling is avoided. L. M. J.

**Measurement of Freezing Point Depressions.** By E. H. Loomis. (*J. Physical Chem.*, 1897, 1, 221—231).—The author compares the method of determining the freezing points of dilute solutions employed by Abegg (Abstr., 1896, ii, 587) with his own (Abstr., 1894, i, 228). In both cases, the convergence temperature is made to practically coincide with the freezing point of the solution by employing a cooling bath, the temperature of which is only very slightly below the freezing point, by protecting the solution from radiation from without, and, finally, by working in a room at a low temperature. The error due to the change of concentration of the solution owing to the separation of ice is reduced to negligible dimensions in both cases by supercooling the solutions to a very small extent. Although these objects are attained in different ways, the two methods are in principle identical.

A comparison of the results obtained shows them to be almost identical with few exceptions; the differences are less than the differences of two sets of observations made by Abegg.

The author concludes, from the experimental data, that the errors in Abegg's determinations are still of the order of 0·02°, but that the principle of the method is free from objection, and consequently the accidental variations could be eliminated by making several series of observations on each substance. At present, notwithstanding the advances made in the experimental methods, few, if any, trustworthy results have been obtained with solutions more dilute than 1/100 normal. T. E.

**Freezing Point depressions of Magnesium Chloride.** By Jacobus H. van't Hoff and H. M. Dawson (*Zeit. physikal. Chem.*, 1897, 22, 598—608).—The authors determined the melting point depression of hydrated magnesium chloride, $MgCl_2 + 6H_2O$, by various compounds, using for the purpose the apparatus described by Meyerhoffer (preceding page). The salt itself melts at 116·67° with the formation of liquid $MgCl_2 + 6·18\ H_2O$ and precipitation of solid $MgCl_2 + 4H_2O$. By means of carbamide and of glycerol, the value 76 was obtained for the normal molecular depression. Potassium chloride gave the same value, the maximum depression obtained corresponding with that due to the saturated solution, $MgCl_2$, 0·026 KCl, 6·18 $H_2O$. Sodium chloride also gave the normal value, the saturated solution being $MgCl_2$, 0·004 NaCl, 6·18 $H_2O$. Hydrated magnesium sulphate gave a low value, and greater difficulty was found in obtaining a constant depression; this was found to be due to the partial, but, on standing, complete, precipitation of the sulphate as kieserite. Potassium sulphate gave, at first, an abnormal value of about 230, that is, three times the normal depression, which may be due to dissociation into three ions, or more probably to the formation of potassium chloride and magnesium sulphate, with later precipitation of kieserite, so that the final value is, as found, that due to the saturated solution of potassium chloride. Kainite gave a depression equal to the sum of those due to magnesium sulphate and potassium chloride. Magnesium bromide

gave a depression of about one-fourth the normal value, the low value being expected from the isomorphism of bromides and chlorides.

L. M. J.

**Influence of Superfusion on the Freezing Points of Aqueous Solutions of Sodium Chloride and Alcohol.** By FRANÇOIS M. RAOULT. (*Compt. rend.*, 1897, **124**, 885—889).—The author has previously shown (*Rev. sci.*, 1886, 603) that the relation between the observed and the real reduction of the freezing point in aqueous solutions is given by the expression $C = C'(1—KS)$ in which $C$ is the true reduction, $C'$ the observed reduction, $S$ the superfusion, and $K$ a coefficient which remains constant for the same apparatus and mode of operating. He also showed that the error due to superfusion could be reduced to 0·01°, a quantity negligible in practice though not in theoretical investigations. It follows that, for the same degree of superfusion, the same apparatus, and the same mode of operating, the ratio $C/C'$ is constant, and it would seem that the error due to superfusion is without influence on the significance of the results (this vol., ii, 11). This view has been widely adopted, but it is not in agreement with the facts.

The author has determined the freezing points of aqueous solutions of sodium chloride and alcohol with the apparatus previously described (*Compt. rend.*, **122**; this vol., ii, 89) and with the precautions already indicated, especially with regard to coincidence between the converging temperatures and the freezing point. Experiments were made with superfusions of about 0·5°, 1·0° and 1·5°, the results being plotted with the superfusions as abscissæ and the observed reduction of freezing points as ordinates. The point at which the curve cuts the axis of the ordinates gives the reduction of freezing point when the superfusion is nil. From the data thus obtained, the value of $K$ in the above expression for a given degree of superfusion can be ascertained: $K = C'—C/C'S$.

The results are given in tabular form. Contrary to the general belief, the value of $K$ is not independent of the concentration, and may become twice as great, as the degree of dilution increases. When $S = 1°$, the value of $K$ may be as much as 2·5 per cent. of the observed reduction, and the ordinary correction in which the value of $K$ is taken as 0·0125 is insufficient, especially in very dilute solutions, the effect of the error being to alter the curve of molecular reductions and raise its point of origin. The true molecular reductions for $S = 0°$ vary in a very different manner in the two cases of sodium chloride and alcohol. With the former, they increase rapidly when the dilution becomes very great, and tend to a maximum value of 37·4, corresponding with ionisation (*loc. cit.*); in the case of the latter, the value of the molecular reduction, 18·3, is independent of the degree of dilution, as Arrhenius predicted.

C. H. B.

**Determination of Molecular Weights. V.** By ERNST BECKMANN (*Zeit. physikal. Chem.*, 1897, **22**, 609—618).—[With C. SCHULTEN]. —When, during freezing, a solid solution separates in place of the pure solvent, the resulting molecular weight is always too high, and in this case the true value may be obtained by the use of a

third compound, which does not form a solid solution, as in the author's experiments on the molecular weight of iodine (Abstr., 1895, ii, 382). Experiments were therefore performed with acetic acid, benzoic acid, and $\alpha$-benzaldoxime for which abnormal molecular weights are also obtained by other methods and are regarded as due to association. Benzene was employed as the solvent and bromoform as the third compound, and in each case the ratios of the quantities of acetic acid, &c., and bromoform in the crystal mass and liquid were equal, so that no solid solution is formed, and the abnormal values for the molecular weights are due to complexes. In the case of thiophen, the results were quite different, the ratio of thiophen to bromoform being much less in the liquid than in the solid, the values for ratio (in solution) ÷ (ratio in crystals) varying from 0·379 to 0·449, so that thiophen and benzene form a solid solution. When this is allowed for in the calculations, the molecular weight of thiophen is obtained as 78·1 in place of 133·3, which is found if no correction is made.

[With H. PFEIFFER].—The molecular weight of selenium as obtained by vapour density determinations decreases from $Se_{2·8}$ at 860 to $Se_{2·08}$ at 1420; it therefore seemed probable that, at ordinary temperatures, a high value would be obtained, and determination of the freezing point of solutions of selenium in phosphorus gave values corresponding with $Se_{7·6}$, a result closely analogous to those obtained with sulphur (Abstr., 1890, 447; 1891, 260).

The author further describes a modification of the form of apparatus previously described (this vol., ii, 88), whereby the electro-magnetic stirrer is avoided by the use of a mechanical stirrer working through an air-proof mercury joint, and a practically similar method due to Kaiser is also appended. L. M. J.

**Exact Cryometry.** By A. PONSOT (*Compt. rend.*, 1896, **123**, 557—559).—A reply to Raoult's criticism of the author's results (this vol., ii, 88).

**Application of the Clapeyron Formula to the Melting Point of Benzene.** By R. DEMERLIAC (*Compt. rend.*, 1896, **122**, 1117—1118). —The change in the melting point of benzene, with a change in pressure of one atmosphere, is calculated by the Clapeyron formula and found to be 0·02936°. The value found experimentally between the limits 1 and 10 atmospheres is 0·0294°. Between these limits of pressure, the formula therefore holds, but it does not apply outside these limits. H. C.

**Verification of the van der Waals Law of Corresponding Conditions.** By ÉMILE H. AMAGAT (*Compt. rend.*, 1896, **123**, 30—35). —In all attempts that have hitherto been made to test the van der Waals law of corresponding conditions, one great source of error and objection has been found in the uncertainty of the determined values for the critical data. In order to avoid this difficulty in the comparison of substances with one another, the author constructs the isothermals of a number of compounds to arbitrary scales of pressure, and reduces the resulting diagrams by photographic process to corresponding scales of pressure. The superposed curves should then show coincidence, and the result is quite independent of the absolutely

determined values of the critical pressure or critical volume. A complete coincidence is, in fact, found for carbonic anhydride, air and ether, and an almost as complete agreement for carbonic anhydride and ethylene. The law of van der Waals is, therefore, in these cases fully confirmed. H. C.

**Van der Waals' Law of Corresponding Conditions and the Determination of Critical Constants.** By ÉMILE H. AMAGAT (*Compt. rend.*, 1896, **123**, 83—86).—The coincidence in the isothermal curves of different substances constructed to corresponding scales of pressure, which has been demonstrated by the author (preceding abstract), renders possible a determination of critical data by comparison of the curves obtained; for the critical points must coincide, and it will therefore be only necessary to read off the co-ordinates of the one system (B) which correspond with the critical co-ordinates of any standard system (A). Thus, taking the critical constants of carbonic anhydride as the standard, those of ethylene, ether, and air are found to be as follows:

| | Carbonic anhydride. | Ethylene. | Ether. | Air. |
|---|---|---|---|---|
| Critical temperature ......... | 31·35° | 8·8° | 195° | −140·7° |
| ,, pressure (in atm.) ... | 72·9 | 48·5 | 36·5 | 35·9 |
| ,, volume ............... | 0·464 | 0·212 | 0·253 | 0·344 |

H. C.

**Liquefaction of Mixtures of Two Gases.** By PIERRE DUHEM (*J. Physical Chem.*, 1897, **1**, 273—297).—The phenomenon considered in this memoir was first observed by Cailletet (*Compt. rend.*, 1880, **90**, 210). A mixture of 1 volume of air and 5 volumes of carbonic anhydride liquefies partially under a moderate pressure, whilst, on increasing the pressure, it again evaporates. The two pressures approach each other as the temperature rises. Analogous observations were afterwards made by van der Waals and by Andrews. The author, in 1888, pointed out that the phenomena might be accounted for by supposing that, for certain concentrations of the gaseous mixture, the dew curve (the curve representing the pressures under which a given gaseous mixture will just deposit liquid at given temperatures) is of such a form that at certain temperatures there are two points on the curve which correspond with the same temperature. Kuenen (*Arch. Néerl*, 1892, **26**, 394), whose measurements were made with the object of testing van der Waals' molecular theory of a fluid consisting of two different compounds, showed that the dew curve really has this form. The pressure first increases with rising temperature up to a certain point, $T$ say, after which it increases with falling temperature, the curve terminating at a point, $\theta$, called the point of folding. Above $T$, no condensation can take place; between $T$ and $\theta$, normal condensation followed by retrograde condensation can occur, whilst below $\theta$ only normal condensation is possible. At the point of folding, $\theta$, the liquid and gaseous mixtures become identical, and at this point the dew curve of the gaseous mixture meets the boiling curve of the liquid mixture of the same composition. Kuenen supposes that these two curves meet so as to form a single line, and that it is always the dew

curve which is cut twice by a straight line at right angles to the temperature axis. This leads to the conclusion that the phenomenon of retrograde condensation must be capable of being observed with every gaseous mixture of the two substances, whereas if the dew curve and the boiling line meet to form a cusp, this is not necessarily the case. By means of considerations of a mathematical nature, which cannot be reproduced in brief, the author concludes that the former view is the correct one, and shows that all the observed phenomena may be deduced from it. T. E.

**Simplified Formula for Calculating the Changes in Density of Liquids with the Temperature.** By PHILIPPE A. GUYE and CHARLES JORDAN (*Bull. Soc. Chim.*, 1896, [iii], 15, 306—308).—Thorpe and Rücker (Trans., 1884, 135) give a relationship between the specific volumes $V$ and $V'$, and the densities $D'$ and $D$ at the temperatures $T'$ and $T$ in the case of any liquid, which may be expressed by

$$\frac{V}{V'} = \frac{D'}{D} = \frac{aT_c - T'}{aT_c - T}.$$

Here $V$ and $D$ are the specific volume and density corresponding with the absolute temperature $T$, $V'$ and $D'$ are the volume and density corresponding with the absolute temperature $T'$, $T_c$ is the critical temperature on the absolute scale, and $a$ is a constant for all substances, of the value 1·995. Since $T_c$ is connected with the boiling point on the absolute scale $T_e$ by the formula $T_c/T_e = 1·55$, substituting in the above $T_e \times 1·55$ for $T_c$, we get

$$\frac{V}{V'} = \frac{D'}{D} = \frac{3·09T_e - T'}{3·09T_e - T}.$$

This holds for liquids the molecules of which contain from 4 to 25 atoms, but with a greater number of atoms in the molecule the constant has a smaller value than 3·09. The authors therefore conclude that for every substance the constant has an independent value $a'$, which could be found for any one substance by making two determinations of $V$ at different temperatures, when $a' = (TV - T'V')/T_e(V - V')$. It is shown that for ethylic butylic succinate, the value $a' = 2·6056$ gives calculated values which are in agreement with the observed for temperatures ranging from 20° to 200°. H. C.

**Partition Coefficients and Abnormal Diffusion.** By GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1897, 22, 483—491).—If a substance is in equilibrium in two different phases, the concentration is in general different in the two, but as the system, either by alteration of pressure or of temperature, approaches its critical state, the partition coefficient approaches the limiting value of unity. This may be illustrated by a solution of triphenylrosaniline in a mixture of benzene and acetic acid (slightly aqueous) at temperatures varying from 0° to the critical temperature 18°, and is deduced theoretically from consideration of the internal pressure of the solutions. The unequal partition of a substance also explains cases of abnormal diffusion, that is, motion of dissolved substance from places of lower to places of higher osmotic pressure. Examples of such cases are given where the liquids employed are methylic or ethylic alcohol and water, and the dissolved

substance, a dye, is originally equally concentrated in both solvents. Alkali-blue diffuses to places of higher osmotic pressure, that is, from the alcoholic to the aqueous layers; sodium triphenylrosanilinetrisulphonate is peculiar, inasmuch as a maximum value for the partition coefficient is obtained for a certain alcoholic-water mixture; methylene-blue behaves in a manner the reverse of that of alkali-blue, diffusing to the more alcoholic layers; nigrosine, indigocarmine and malachite-green behave similarly to alkali-blue. Iodine was found to diffuse from ether or amylic alcohol to acetone, and experiments with sugar solutions and water showed that dyes diffuse to the layers poorer in sugar. By the use of two dyes, such as methylene-blue and nigrosine, two opposite diffusion streams can be set up. Similar differences are observed with different membranes, thus a pig's bladder dissolves far more methylic alcohol than ether, but the reverse obtains with caoutchouc, so that the diffusion streams in mixtures separated by these membranes can vary with the membrane employed. L. M. J.

**Equilibrium between Amalgams and Electrolytes.** By A. OGG (*Zeit. physikal. Chem.*, 1897, 22, 536—538).—Mercury and an aqueous solution of silver nitrate react until a final equilibrium is reached between the amalgam formed and the solution of silver and mercurous nitrates, whilst, similarly, between a silver amalgam and mercurous nitrate the reverse action occurs. In this case, if the mercury be present in excess, its active mass may be regarded as constant, whilst that of the silver is proportional to its concentration in the amalgam, and hence, as the salts are also approximately equally dissociated at equal concentrations, the equilibrium constant is given by the equation $a = k\ b\ c$ where $a$ and $b$ are the concentrations of the silver and mercury salts in the solution, and $c$ that of the silver in the amalgam. This relation was tested by a series of 10 experiments at 82°, in which the concentration of the silver varied from 0·004 to 0·05, the values for $k$ being in close accord. The heat of formation of the amalgam was calculated by the use of Nernst's expression,

$$q = 4{\cdot}56 \log k_2/k_1, T_1T_2/(T_2 - T_1),$$

the values obtained from experiments at 15°, 53°, and 90° varying from 2500 to 3400 cals. L. M. J

**Chemical Equilibrium, &c., of Metallic Mixtures.** By WALTHER NERNST (*Zeit. physikal. Chem.*, 1897, 22, 539—542).—In the case of the equilibrium of a homogeneous metallic mixture with an electrolytic solution, the necessary condition is $RT/n_1 \cdot log P_1/p_1 = RT/n_2 \cdot \log P_2/p_2$ where $P_1$ and $P_2$ are the solution tensions of the metals, $p_1$ and $p_2$ the osmotic pressures of their metallic ions in the solutions, and $n_1$ and $n_2$ the equivalency of the metals. This reduces to $(P_1/p_1)^{\frac{1}{n_1}} = (P_2/p_2)^{\frac{1}{n_2}}$, a result shown by Ogg (preceding abstract) to hold in the case of silver and mercury, where $n_1 = n_2$. The potential difference between the alloy and the liquid is given by either of the values $RT/n \cdot \log P/p$, and the quantities of metals dissolved or precipitated by a current may differ, the ratio of the amounts for an infinitely small current being in the case of equivalent metals equal to the ratio of their ion concentrations. L. M. J.

**Influence of Water on the Solubility of Hydrated Compounds in Alcohol and Ether.** By EYVIND BÖDTKER (*Zeit. physikal. Chem.*, 1897, 22, 505—514).—In order to study the lowering effect of water on the solubility of salts in alcohol, the author determined the ratio of the concentrations of water and anhydrous salts in the case of alcoholic solutions of cupric chloride and cobalt chloride. These concentrations (grams per 5 c.c.) being represented by $C_w$ and $C_s$, it was found in solutions of the copper salt that the value $C_wC_s^2$ does not yield a constant, so that dissociation $CuCl_2 2H_2O \rightleftarrows CuCl_2 + 2H_2O$ does not take place. The product $C_wC_s$ is approximately constant for small values of $C_w$, but at higher concentrations $C_sC_w^{\frac{1}{2}}$ gives a more satisfactory value, so that the results indicate a dissociation represented by $CuCl_2,2H_2O \rightleftarrows CuCl_2,H_2O + H_2O$, with the formation of double water molecules at higher concentrations. Cobalt chloride gave analogous results indicating a dissociation, $CoCl_2,6H_2O \rightleftarrows CoCl_2,5H_2O + H_2O$, with association of water molecules. Hydrated calcium chloride is also more soluble in concentrated than in slightly aqueous alcohol, but with the other salts examined the solubility is too small for accurate measurement. The behaviour of oxalic acid in aqueous ether gave anomalous results, which indicate a greater solubility of water in ether containing oxalic acid than in pure ether, this being, in the author's opinion, due to the existence in the ethereal solution of a compound of oxalic acid and water. L. M. J.

**New Method Proposed by Etard for the Curve Representation of the Solubility of Salts.** By E. LENOBLE (*Bull. Soc. Chim.*, 1896, [iii], 15, 54—58).—According to Etard, if the solubility $y$ of a salt is expressed by the percentage of salt in the solution at any temperature $x$, then $y = a + bx$, where $a$ and $b$ are constants, and the solubility curve is a straight line. In this case, if $y$ is transformed from the Etard notation to that of Gay-Lussac, and the solubility $Y$ calculated in terms of the amount of salt dissolved by 100 parts of the solvent, $Y = 100(a + bx)/(100 - bx - a)$, and the solubility curve in this case should be hyperbolic. The author tests this conclusion in the case of potassium chlorate, but finds that it does not hold, the solubility curve being at least one of the fourth degree. Etard's method of representation does not give a straight line, but a more complex curve. H. C.

**Relation between the Velocity of Inversion and the Concentration of the Hydrogen Ions.** By WILHELM PALMAER (*Zeit. physikal. Chem.*, 1897, 22, 492—504).—Previous experiments have shown that the velocity of inversion of sugar by acids is not strictly proportional to the concentration of the hydrogen ions, but decreases more rapidly when the dilution is great, and the author has, therefore, investigated the cause of this at concentrations varying from N/10 to N/1000. Three important sources of error were found to affect the results: (1) neutralisation of the acid by the alkali of the glass; (2) impurity in the sugar; (3) the birotation of the glucose. The impurity found in commercial sugar was largely chalk, and hence, even if present to a very small extent, its importance increases with dilution, so that it is necessary to use sugar as pure as possible, and

yielding the minimum of ash; that employed by the author left a residue of 0·002 per cent. The effect of alkali in the glass was avoided by the use of platinum vessels, and the birotation was allowed for in the calculations. When these precautions were taken, (the required velocity) ÷ (concentration ratio) was found to be practically constant, giving a decrease of about 10 per cent. from N/10 (in glass vessels) to N/100 (platinum), and afterwards remaining constant within experimental errors, the limits for five experiments being 1863 and 1844. L. M. J.

## Inorganic Chemistry.

**Formation of Hydrogen from Iron and Water.** By W. LETTERMANN (*Chem. Centr.*, 1896, i, 952—953; from *Diss. Giessen*).—In investigating the action of steam on hot iron, a porcelain tube containing the iron shavings, and packed at the ends with broken porcelain to ensure a uniform temperature of the gases, was employed. Instead of steam, nitrogen saturated with steam was used, as this method admits of the ready calculation of the weight of water sent over, and the tension of the steam, and also of easy regulation of the velocity of the stream. The nitrogen was sent from a gas-holder, at constant pressure, through flasks containing alkaline pyrogallol, and then into a Varrentrapp's bulb apparatus completely immersed in a water bath; the bulb was weighed before and after the experiment. Before entering the tube, the mixed gases were superheated by passing through a steel tube heated to below 300°. The temperatures were determined by means of the bulb-shaped platinum pyrometer of P. Freyer and V. Meyer (Abstr., 1892, 680). After traversing the tube, the gases pass through a U-tube immersed in water, in which most of the excess of water collected, then through a calcium chloride tube, and finally into a gas-holder with constant mercury level. Other conditions remaining the same, the formation of hydrogen was found to decrease with increase of the speed of the nitrogen stream, particularly at lower temperatures. More hydrogen is evolved at higher temperatures than at lower, the action beginning at 300°, and giving the best yield at 800°. E. W. W.

**Commercial Production of Tellurium.** By J. FARBAKY (*Zeit. angw. Chem.*, 1897, 11—18).—A method is described whereby tellurium is produced on the large scale from gold tellurium ores. The ore is slowly thrown into boiling concentrated sulphuric acid, when lead, copper, zinc, tellurium, and also a portion of the silver compounds present go into solution, gold and silicic acid remaining undissolved. The product is then heated with water containing from 10 to 15 per cent. of hydrochloric acid, when the latter precipitates the dissolved silver and dissolves the hydrated tellurium oxide precipitated by the water. On filtering, a residue of gold and silver is obtained which is worked up separately. Sulphurous anhydride is passed through the filtrate, and as this takes place in sulphuric or hydrochloric acid solu-

tion, only tellurium and selenium are thrown down. This residue is found to contain from 72—85 per cent. of tellurium, and after a repetition of the process, the percentage is increased to 97—98. The crude powder is melted and cast in moulds. A. W. C.

**Oxidation of Nitrogen by means of Electric Sparks or the Electric Arc.** By FRANZ VON LEPEL (*Ber.*, 1897, **30**, 1027—1030. Compare Lord Rayleigh, Trans., 1897, 181).—The best yield of nitric acid is obtained under the following conditions. The electrodes are placed in the lower expanded extremity of a perpendicular glass tube of 2—3 litres capacity. The lower cathode is in the form of a flat plate, whilst the upper anode is pointed. A moderately rapid stream of air is kept passing through the apparatus, and a fine liquid spray is forced in from above, this dissolves the nitric acid as it is formed, and the acid solution can be drawn off below. A solution containing 0·56 per cent. of nitric acid was obtained with a cylindrical vessel of 1·75 litres capacity, whilst with a spherical vessel of 1 litre capacity the amount of acid was only 0·31 per cent.

The yield of acid increases more rapidly with an increase in the strength of the current than with an increase in the length of the sparks; if the air is not kept in motion, the nitric peroxide is destroyed almost as quickly as formed.

The amount of air present, the nature of the electrodes, and also the nature of the liquid spray, greatly affect the yield of acid. Liquids which can act as oxygen carriers, for example, magnesium sulphate or calcium permanganate, increase the yield of acid (compare L. Meyer, Abstr., 1888, 216); ozonised air and Röntgen rays, however, appear to decrease the yield. J. J. S.

**Hyponitrous Acid.** By EDWARD DIVERS (*Annalen*, 1897, **295**, 366—370. Compare this vol., i, 67, and ii, 25).—The author claims priority in the discovery of the hyponitrites, which Hantzsch and Kaufmann attribute to Maumené (*loc. cit.*). M. O. F.

**Constitution of Nitramide.** By JOHANNES THIELE (*Annalen*, 1897, **296**, 100—110).—The formula, $NH_2{\cdot}NO_2$, adopted by Thiele and Lachmann in representing nitramide (Abstr., 1896, i, 208), has been opposed by Hantzsch, who has endeavoured to establish a stereoisomeric relationship between this substance and hyponitrous acid, $HO{\cdot}N{:}N{\cdot}OH$ (this vol., ii, 26). The present paper is devoted to criticism of Hantzsch's view, support of the original formula being derived from the difference in electrical conductivity of nitramide and hyponitrous acid (Baur, this vol., ii, 358) and also from the production of dimethylnitramine, $NMe_2{\cdot}NO_2$, when diazomethane acts on nitramide, it having been shown that this agent exhibits a marked tendency to yield oxygen methyl ethers (compare Degner and von Pechmann, this vol., i, 264).

M. O. F.

**Nitramide.** By ARTHUR R. HANTZSCH (*Annalen*, 1897, **296**, 111—119. Compare foregoing abstract).—A reply to the criticisms of Thiele and Baur on the author's view of the constitution of nitramide. M. O. F.

**Hypophosphorus Oxide.** By J. ADOLPHE BESSON (*Compt. rend.*, 1897, **124**, 763—765).—Hydrogen phosphide has no action on phosphorus oxychloride at its boiling point, but in presence of a small quantity of hydrogen bromide interaction takes place at about 50°, and continues until the hydrogen bromide is all volatilised as phosphonium bromide. Hydrogen chloride is liberated and a reddish-yellow solid is formed. The same product is obtained by the action of hydrogen phosphide on the bromine derivatives of phosphorus oxychloride and also by the action of phosphonium bromide on phosphorus oxychloride in sealed tubes at 50°. Since the two substances do not interact at the ordinary temperature, the phosphonium bromide is conveniently obtained by passing dry hydrogen phosphide into a solution of carefully dried hydrogen bromide in phosphorus oxychloride.

The red product retains chlorine tenaciously and is best purified by heating it with phosphorus oxychloride in sealed tubes at 100° for several hours, repeatedly extracting with boiling carbon bisulphide, and then washing with boiling water, and afterwards drying in a vacuum at first over sulphuric acid at the ordinary temperature and afterwards at 100°. It then has the composition $P_2O$ and is a reddish-yellow, very light, pulverulent solid, stable in presence of air up to 100°, but taking fire when heated more strongly. When heated at about 135° in a vacuum, it slowly loses oxygen. Nitric acid acts on it in much the same way as on phosphorus, and chlorine also acts on it with incandescence at the ordinary temperature. In presence of carbon tetrachloride, chlorine converts it into phosphorus tri- or pentachloride, without any formation of oxychloride; bromine, on the contrary, converts it into a mixture of the oxybromide with the tri- and penta-bromides, whilst iodine converts it into the di-iodide $PI_2$ without any formation of oxyiodide. The oxide yields no acid when heated with water or a solution of an alkali, and hence it cannot be regarded as a true hypophosphorous anhydride but it stands to hypophosphorous acid and the hypophosphites in the same relation as nitrous oxide to hyponitrous acid and the hyponitrites.

In addition to hypophosphorous oxide, the action of phosphonium bromide on phosphorus oxychloride yields pyrophosphoryl chloride $P_2O_3Cl_4$ and metaphosphoryl chloride, $PO_2Cl$.

Phosphonium iodide acts on phosphorus oxychloride below 100° with liberation of hydrogen chloride and formation of the iodide $P_2I_4$, red phosphorus, which obstinately retains iodine, and metaphosphoryl chloride.

C. H. B.

**Diamonds in Steel.** By LEON FRANCK [and, in part, ETTINGER] (*Chem. Centr.*, 1896, ii, 573; from *Stahl u. Eisen*, **16**, 585—588).—Various kinds of steel were treated, as Moissan describes, with nitric, hydrofluoric, sulphuric acids, &c. From unhammered steel, an iron-carbide, $FeC_4$, a carbide crystallising in octahedra, and probably of the composition $Fe_3C_2$, and a number of modifications of carbon were obtained. Amongst the last, minute, well-formed octahedra, which sank in methylenic iodide and on combustion left little ash, were observed. From rolled steel, fragments of diamonds with distinct diamond structure were obtained in small quantity. Examination of fifty

varieties of steel led only in few cases to negative results. Higher magnifying powers revealed more numerous diamonds. The very small diamonds only visible under powers of from 2500 to 3000 were apparently attacked by strong oxidising agents. E. W. W.

**Compounds of Ammonia and of Methylamine with Halogen Salts of Lithium.** By J. BONNEFOI (*Compt. rend.*, 1897, 124, 771—773).—At $-18°$, dry lithium chloride rapidly absorbs ammonia, and forms the compound $LiCl,4NH_3$, the dissociation curve of which has been determined between $-12°$ and $+18°$. Its dissociation pressure is 760 mm. at 13·3°. At 18°, the compound $LiCl,3NH_3$ is formed, and its dissociation pressure is 760 mm. at 57·5°. At 63°, the compound formed is $LiCl,2NH_3$, and at 85° $LiCl,NH_3$. In dilute solutions, ammonia has no action on lithium chloride, and the ammoniacal lithium chlorides are completely dissociated by water in the proportion of 2 litres to 1 gram-molecule of lithium. The heat of dissolution of the compound $LiCl,3NH_3$ at 15° is $+0·37$ Cal., and since that of lithium chloride is $+8·43$ Cal., it follows that $LiCl + 3NH_3$ gas develops $+34·46$ Cal. $(11·48 \times 3)$. The corresponding values for the compound $LiCl,2NH_3$ are $+2·67$ Cal. and $+23·36$ Cal. $(11·68 \times 2)$ respectively. The conversion of $LiCl,2NH_3$ into $LiCl,3NH_3$ develops therefore $+11·10$ Cal.

Comparing these values with Isamberts results (Abstr., 1878, 697), it follows that the heat of combination with ammonia is lower the more dissociable the compound. Clapeyron's formula gives $+11·09$ Cal. for the mean heat of combination with $NH_3$, and this agrees well with the experimental results.

Lithium chloride also absorbs methylamine, and at 0° forms the compound $LiCl,4NH_2Me$, the dissociation pressure of which is 760 mm. at $+30°$.

Dry lithium bromide forms the compound $LiBr,4NH_3$ at $-18°$, and its dissociation pressure is 760 mm. at 63°. C. H. B.

**Silver Diphosphide.** By A. GRANGER (*Compt. rend.*, 1897, 124, 896—898).—When phosphorus vapour is passed over finely-divided silver heated at 400°, combination takes place, and if the tube is cooled suddenly whilst still full of phosphorus vapour, a product of definite composition, *silver diphosphide*, $AgP_2$, is obtained. It is soluble in nitric acid, and is attacked by chlorine, bromine, and aqua regia. When heated in a current of inert gas at the temperature of its formation, the diphosphide is completely decomposed. No combination of silver with phosphorus takes place, and hence the metal, like gold, has the peculiarity of combining with phosphorus at 400°, giving it up at 500°, and again retaining it at 900°.

Silver is not attacked by phosphorus trichloride at any temperature below that at which the silver phosphide is decomposed, and the products are silver chloride and phosphorus. The phosphide can, however, be obtained by the action of phosphorus on silver chloride at 300—400°.

The so-called silver sesquiphosphide of Schrötter was probably identical with this diphosphide. C. H. B.

**Magnesium Phosphates.** By HEINRICH STRUVE (*Zeit. anal. Chem.*, 1897, **36**, 289—298).—The author has prepared three new compounds of phosphoric acid and magnesia. The first, which has the formula $2MgO,P_2O_5 + 7H_2O$ is obtained by dissolving ignited magnesia in boiling orthophosphoric acid until the acid reaction has nearly disappeared. It separates from the boiling solution as a heavy, white, crystalline powder, which under the microscope is seen to consist of rhombs and six-sided plates, showing double refraction. The air-dried substance loses no water at 100°. On ignition, it becomes anhydrous without change of form. A salt of the same composition has been prepared by Hager by mixing highly concentrated solutions of sodium phosphate and magnesium sulphate, and exposing the gelatinous magma to a low temperature (8°), when it contracts to a crystalline sediment.

The second salt, $2MgO,P_2O_5 + 15H_2O$, is prepared by adding to a dilute solution of sodium phosphate sufficient magnesium sulphate to redissolve the precipitate formed at first; it separates gradually in large, colourless, striated, prismatic crystals. At 100°, these crystals lose $9H_2O$, and the whole on ignition. The third salt, which when air-dried has the same composition, is obtained by precipitating a moderately dilute solution of magnesium sulphate with one of sodium phosphate, and passing carbonic anhydride through the magma until complete solution takes place. After discontinuing the passage of the gas, the salt separates in small, colourless, prismatic crystals. It differs from the second salt in losing only $8H_2O$ at 100°, or more slowly at atmospheric temperature. When preserved in a stoppered bottle, it decomposes into the first salt and water. The solubility of the three salts is 1 part in 4000 of water. All three acquire a brownish-yellow colour, and strongly marked striation when dehydrated. The striation is undoubtedly due to the formation of tubular cavities, as is shown by the way in which the dehydrated crystals absorb neutral dyes, such as magenta.

M. J. S.

**Solubility of Mercuric Chloride.** By DOUGLAS MCINTOSH (*J. Physical Chem.*, 1897, **1**, 298—300).—Étard (Abstr., 1892, 558) found that the curve of solubility of mercuric chloride consists of two branches which intersect, the temperature at which the intersection occurs depending on the solvent used. This should not be the case if the change in the slope of the curve is due to a change of one modification of solid mercuric chloride into another. The author finds that when methylic alcohol is used as solvent, $HgCl_2$ crystallises out at temperatures above 40°, $HgCl_2,CH_3\cdot OH$ separating below 35°. The intersection of the two branches of the curve occurs at 38·8°. The addition of water to the alcohol depresses the transition temperature. The author considers it probable that mercuric chloride forms compounds similar to the above with other organic solvents.

T. E.

**Effect of a High Temperature on Copper, Bismuth, Silver, Tin, Nickel, and Cobalt Sulphides.** By A. MOURLOT (*Compt. rend.*, 1897, **124**, 768—771).—When heated in the electric furnace, cupric sulphide is converted into cuprous sulphide, and the latter fuses and is reduced to metallic copper. Cupric sulphate is also reduced to the metal under the same conditions. Bismuth sulphide is readily

reduced. Silver sulphide melts and is readily reduced; but reduction is not quite complete, and the condensed drops of the volatilised metal retain traces of sulphur. Stannous sulphide, when not very strongly heated, becomes crystalline, but at a higher temperature volatilises. The condensed product has, however, still the composition of stannous sulphide, which, therefore, is a remarkably stable compound. Nickel sulphide is first converted into a non-crystalline, bronze-yellow subsulphide, $Ni_2S$; and this, when more strongly heated, loses all its sulphur, the reduced metal combining with about 6 per cent. of carbon, about 5·5 per cent. existing as graphite. Cobalt sulphide is readily obtained by heating the anhydrous sulphate in a small electric furnace; at a higher temperature, it loses all the sulphur, and the metal combines with about 4·7 per cent. of carbon, 4·5 per cent. being in the form of graphite. C. H. B.

Fergusonite Metals; Philippium. By M. Marc Delafontaine (*Chem. News*, 1897, 75, 229—230).—To extract philippium, the ore is treated in quantities of 500 grams in a leaden vessel with 1500 grams of strong hydrofluoric acid, the products are repeatedly treated with water, and the insoluble fluorides decomposed in a platinum dish with sulphuric acid; sodium dioxide is then added to oxidise any uranous salts in the solution, the earths are precipitated by oxalic acid, and the ignited precipitate treated with nitric acid. Philippium may be separated from the mixed nitrates by fractional decomposition by heat, or by fractional precipitation with dilute ammonia or with potassium hydrogen oxalate, the separation depending in all cases on the lower basic energy of philippium. The author prefers the fractional decomposition by heat: the mixture of nitrates is heated until quiet fusion has ensued for some minutes, and when cool the red, vitreous mass is treated with water, the treatment of the soluble portion being repeated until no coloured residue is left. If all the residue dissolves, the solution is digested with dilute ammonia in a warm place for some hours, and subsequently decomposed at a higher temperature. The sub-salts obtained in this way are subjected to new series of decompositions until a bright, orange-yellow, basic nitrate is obtained, which dissolves slowly in moderately dilute nitric acid to a deep orange-red, transparent solution. Philippium forms philippous and philippic salts corresponding with a white and an orange oxide. The first salts are colourless, stable, and crystallise well, and do not seem to give any absorption spectrum in solution. Of the *potassium philippous* salts:—the *sulphate* is soluble in a saturated solution of potassium sulphate; the *formate* crystallises very slowly from a syrupy solution in fibro-radiated masses; the *oxalate*, dried at 130°, yields on ignition 51·5 per cent. of orange-coloured oxide; the *nitrate* is colourless and crystalline, but, on fusion, yields a reddish glass, partially soluble in water, and apt to form a solution difficult to filter. *Philippic oxide* is deep orange-red, the moist *hydroxide* being light yellow; with cold, moderately dilute nitric acid, it gives a yellow solution, with the strong acid it effervesces, becomes hot, and yields colourless philippous nitrate; with hydrochloric acid, chlorine is evolved, and it gives proto-salts; it is dissolved by other acids when boiled in the presence of alcohol.

Philippium is more closely allied to cerium and terbium than to any other of the cerium metals; but the behaviour of the salts set forth above distinguishes it even from these metals. D. A. L.

**Aluminium Amalgam.** By DMITRI P. KONOWALOFF (*Chem. Centr.*, 1896, ii, 338; from *Pharm. Zeit. Russ.*, **35**, 328—329).—The use of aluminium amalgam as a reducing agent has been recommended by Hans Wislicenus and Kaufmann, as in many cases it produces insoluble products, hence no new substances are introduced into solution. The author has investigated the action of water on this amalgam. The amalgam prepared as described by the authors mentioned above, after washing with alcohol, ether and light petroleum, was dried in a current of dry air. It does not act on alcohol containing only a little water, even on boiling, but by gradually increasing the amount of water until it reaches about 11·36 per cent. a solution is obtained which is attacked by the amalgam on boiling, with liberation of hydrogen. Acetic acid containing only 0·1 per cent. of water is attacked by the amalgam with evolution of more hydrogen than corresponds with the water present, but after the action there is no perceptible alteration in the freezing temperature of the acid; with larger quantities of water, however, the freezing point becomes higher, owing to the production of basic aluminium acetate which withdraws a portion of the water.

E. W. W.

**Formation of Manganese Compounds.** By ODIN T. CHRISTENSEN (*Chem. Centr.*, 1896, ii, 151; from *Oversigt Videnskabernes Selskabs Forhandlinger*, 1896, 94).—The author did not succeed in preparing a manganese alum. Manganic salts are conveniently prepared by a method which depends on the oxidation of manganous salts by permanganic acid: $Mn_2O_7 + 8MnO = 5Mn_2O_3$. Thus manganic phosphate is obtained by warming a saturated solution of orthophosphoric acid, to which a little acetic acid is added, with manganese sulphate and a saturated solution of potassium permanganate. Manganous salts easily become oxidised in alkaline solution, and reduce Fehling's solution with separation of cuprous oxide and formation of manganic tartrate. This solution can be used repeatedly as an oxidising agent, since after reduction it reabsorbs oxygen from the air. Ignited manganese sesquioxide is attacked by organic acids such as lactic and pyrotartaric acids with rise of temperature, and in the case of the former an odour of acetaldehyde becomes apparent, and a manganous salt is formed.

E. W. W.

**Preparation of Pure Iron.** By HICKS and O'SHEA (*Chem. Centr.*, 1896, i, 293; from *Electrician*, 1895, 843).—Pure iron is obtained by electrolysing a 5 per cent. solution of ferrous chloride to which ammonium chloride has been added in quantity sufficient to form the double compound $FeCl_2,2NH_4Cl$. Any ferric chloride which on electrolysis would form ferric hydroxide, is removed by shaking with pure iron in powder. During electrolysis, the content of iron must not be allowed to become less than 20 to 30 per cent. of the original quantity, and the cathode should be kept completely immersed in the solution. The thin copper plate which serves as cathode is cleaned by

washing with dilute nitric acid, rubbing with cotton wool and fine sand, washing with potassium cyanide solution and finally with water. Swedish iron plate, containing 0·027 per cent. of sulphur and 0·049 per cent. of carbon, is used for the anode, and is placed in a porous cell in order to prevent the spongy carbon separated at the anode from reaching the cathode. The sulphur goes into solution as sulphate, and must be removed from time to time with the anode liquor. A current of 0·08 to 0·2 ampère per 100 sq. cm. of cathode surface at about 0·7 volt. is employed. The iron is obtained as a compact, silver white precipitate of velvety appearance. E. W. W.

**Production of Iron Carbide by Direct Combination of Iron and Carbon.** By HENRI MOISSAN (*Compt. rend.*, 1897, **124**, 716—722).—The researches of several previous observers have shown that fused or annealed steel contains a crystalline carbide of the composition $Fe_3C$, and the author has extended these observations to cast iron and the products of the direct action of carbon on iron.

Blooms from three different high blast furnaces were examined in the usual way, but no traces of diamonds could be discovered.

Pure iron was heated with sugar-charcoal in the electric furnace; the mass became more and more viscous as the temperature increased, but regained its limpidity as it cooled, and the cold metal was found to contain only about 1 per cent. of carbon in combination. It would seem, therefore, that carbon and iron combine at a high temperature, but the compound dissociates as the temperature falls. Nickel behaves similarly. It had been observed in the preparation of the diamond that the interior of the metal contained brilliant crystals similar to iron boride or iron silicide. It seemed that the conditions necessary to ensure combination are to avoid complete saturation of the iron by carbon and the formation of graphite; Swedish iron, therefore, was heated in a carbon crucible for 3 minutes with an arc from a current of 900 ampères and 600 volts., and the fused mass cooled quickly by pouring it into water. The product was a very hard and brittle metal, often very highly crystalline, and containing very little graphite, but from 3 to 4 per cent. of combined carbon. In order to isolate any carbide that might be present, the author employed (*a*) the electrolytic method of Mylius, Foerster and Schoene (this vol., ii, 39), and (*b*) the action of very dilute acids out of contact with air. With small quantities of carbide, a stronger acid may be used. Normal nitric acid yields the carbide mixed with a little carbon, whilst the half-normal acid yields the practically pure carbide. In order to remove the small quantity of carbon and liquid hydrocarbons that may be mixed with the carbide, the latter is treated with nitric acid as free from water as possible, and is afterwards poured into a large quantity of water, washed with alcohol and ether, dried at 100° in a current of carbonic anhydride, and allowed to cool in the gas. Instead of the treatment with nitric acid, the impure carbide may be boiled with a 10 per cent. solution of chromic acid.

The iron carbide thus obtained forms brilliant white crystals of the composition $Fe_3C$; sp. gr. = 7·07 at 16°. It seems to be identical with the carbide present in steel (*loc. cit.*), and is not acted on by oxygen

at the ordinary temperature, although it is somewhat rapidly decomposed by moist air containing carbonic anhydride. When heated, it ignites more easily the finer its state of subdivision, and when very finely divided ignition takes place in air below 150°. It becomes incandescent in sulphur vapour at about 500°, in chlorine below 100°, in bromine vapour at about 100°, and is decomposed by iodine, at a red heat, without incandescence. Hydrogen chloride decomposes it at about 600° with liberation of hydrogen containing a small quantity of hydrocarbons. Concentrated nitric acid has no action on even the finely divided carbide, but on adding a small quantity of water decomposition takes place readily. Dilute acids attack the carbide less rapidly than they attack metallic iron. When heated with dilute hydrochloric acid in sealed tubes, the carbide is decomposed with liberation of a mixture of hydrogen and methane, the proportion of the latter being higher the more concentrated the acid. Water and concentrated solutions of sodium chloride or magnesium chloride have no action on the carbide at 150°. C. H. B.

**Metastannyl Chloride.** By RODOLPHE C. ENGEL (*Compt. rend.*, 1897, **124**, 765—768).—When sticks of tin, about 5 mm. in diameter, are immersed in nitric acid of sp. gr. 1·3 or 1·4, a reaction takes place without any notable rise of temperature, and the product when washed with water and dried in the air has the composition $(SnO_2)_n(H_2O)_{2n}$; 400 grams of this product is mixed with 100 c.c. of hydrochloric acid of 22° B., and after about 15 minutes solution is complete; the gummy-looking mass is then diluted with water and filtered. If now the filtered liquid is mixed with an equal volume of hydrochloric acid, a finely-divided, amorphous, white precipitate is formed, but settles very slowly. The supernatant liquid contains some stannic chloride, and it follows that the metastannic acid prepared in the manner described is mixed with some stannic acid. The precipitate, when washed with hydrochloric acid of 22° B. diluted with its own volume of water, and dried first on unglazed porcelain, and afterwards in a vacuum over sulphuric acid and potassium hydroxide, agglomerates to translucent, deliquescent masses, which dissolve in small quantities of water or absolute alcohol. The concentrated aqueous solution can be diluted with water if a small quantity of hydrochloric acid is added previously. An excess of hydrochloric acid produces a precipitate; the addition of water without acid also gradually produces a gelatinous precipitate, which, after being washed and dried, will recombine with hydrochloric acid to reproduce the original compound. The soluble chloride has the composition $Sn_5O_9Cl_2,4H_2O$, and the gelatinous precipitate produced by water is the metastannic acid of Fremy, $Sn_5O_{11}H_2,4H_2O$.

It follows that the chloride obtained in the manner described is metastannyl chloride. Stannic chloride in aqueous solution is gradually converted into the metastannyl chloride, which differs completely from the ordinary oxychlorides, such as are formed by dissolving stannic acid in a solution of stannic chloride. The oxychlorides, for example, are not precipitated by hydrochloric acid, but are converted into stannic chloride. Dilute sulphuric acid does not precipitate solutions of metastannyl chloride, and it thus differs from the $\beta$-chloride.

The author's experiments indicate the existence of a second metastannyl chloride corresponding with a second metastannic acid, and this will be described in a subsequent paper. C. H. B.

**Crystalline Thorium Nitrate.** By OTTO FUHSE (*Zeit. angw. Chem.*, 1897, 4, 115—116).—When a solution of thorium nitrate is evaporated and allowed to crystallise in a warm place, large, well-formed crystals belonging to the quadratic system are obtained. They contain $6H_2O$. A. W. C.

**Separation of Thoria from Zirconia.** By M. MARC DELAFONTAINE (*Chem. News*, 1897, 75, 230).—The powdered ore or oxides is fused in a platinum crucible with twice its weight of potassium hydrogen fluoride; the zirconia is extracted from the solidified mass in the form of $K_2ZrF_6$, by means of boiling water containing a few drops of hydrofluoric acid; the insoluble fluorides, on treatment with sulphuric acid and ignition below a dull, red heat, yield sulphates of thorium, cerium, and other earths; these are dissolved in water, precipitated by oxalic acid, and the oxalates treated with saturated hot ammonium oxalate, which dissolves the thorium salt. D. A. L.

**Bismuth Dichloride.** By VICTOR THOMAS (*Bull. Soc. Chim.*, 1897, [iii], 15, 758—760).—When bismuth dichloride is heated in air or in nitric oxide, the products are identical with those which would be formed from a mixture of bismuth with the trichloride. This is in agreement with Schneider and Weber's statement, that on heating the dichloride alone, it breaks up into the trichloride and the metal.

M. W. T.

**Action of Air and Nitric Peroxide on Bismuth Iodide and Bromide.** By VICTOR THOMAS (*Bull. Soc. Chim.*, 1897, [iii], 15, 760—762).—The author has already shown that bismuth trichloride in presence of nitric peroxide in the cold, produces a nitro-chloride, which, when heated, decomposes, forming the oxychloride BiOCl.

With the tribromide and triiodide in the cold, the oxybromide and trioxide are formed respectively. In the presence of air, the trihaloids form the corresponding oxy-compounds. M. W. T.

## Physiological Chemistry.

**Hammerschlag's Method of Estimating the Specific Gravity of Blood and Serum.** By LEO ZUNTZ (*Pflüger's Archiv*, 1897, 66, 530—543).—Hammerschlag's method consists in placing a drop of blood in a mixture of benzene and chloroform, and then adding more of one or the other reagent until the drop neither falls nor rises; then the specific gravity of the mixture is taken. The method gives very inconstant results, because diffusion occurs between the blood and the reagents; they and a large number of other possible reagents which were tried are therefore not indifferent either to blood or serum.

W. D. H.

**The Antagonism of Substances in the Blood which accelerate and hinder Coagulation.** By KARL SPIRO and ALEXANDER ELLINGER (*Zeit. physiol. Chem.*, 1897, **23**, 121—159).—The circulating blood is believed to contain antagonistic substances which respectively hinder and hasten coagulation. In shed blood, the latter get the upper hand. In 'peptone blood' and 'leech extract blood,' there is an increase of the hindering substances; and immunity to peptone injection is caused when the hastening substances are no longer overbalanced in this way. Nuclein, on the other hand, causes intravascular coagulation by producing a preponderance of the hastening substances. The question of the nature of these substances is hardly touched on, but an analogy is drawn between them and toxins and antitoxins. W. D. H.

**Freezing Point of Milk.** By J. WINTER (*Compt. rend.*, 1897, **124**, 777—778).—Polemical, in reply to Bordas and Génin.

**Non-identity of Lipases of Different Origin.** By MAURICE HANRIOT (*Compt. rend.*, 1897, **124**, 778—781).—Solutions of the serum and of the pancreatic juice of the dog were prepared so that both had the same hydrolysing effect on monobutyrin in presence of the same excess of sodium carbonate. When, however, they were exactly neutralised, and left in contact with monobutyrin for 20 minutes, the quantity of acid liberated by the serum solution was nearly twice as much as that liberated by the pancreatic solution. It follows that the sero-lipase acts energetically in an acid medium, whilst the activity of pancreato-lipase is greatly reduced under the same conditions.

If solutions are prepared of equal activities at 15°, the activity of the sero-lipase becomes half as great again at 30° and twice as great at 42°, whereas the activity of pancreato-lipase remains constant through the same interval of temperature. Further, the sero-lipase solution retains its activity for several months, whilst the pancreato-lipase solution rapidly alters, and loses its activity after a few days.

Direct experiments show that the blood of the eel contains the same lipase as the blood of the horse, but in much larger quantity. The activity of lipase from the serum of the horse increases with the alkalinity of the solution, and with 2 grams of sodium carbonate per litre, it may become four times as great as under normal conditions.

Since the ferment of the blood that has the power of rendering proteids soluble has its activity increased by the presence of alkali, it follows that the smallest variations in the alkalinity of the blood, whether due to natural causes or produced by the administration of such medicines as sodium hydrogen carbonate, must exert an appreciable effect on the processes of assimilation. C. H. B.

**Estimation of Sugar.** By EDUARD PFLÜGER (*Pflüger's Archiv*, 1897, **66**, 635—640).—Argutinsky has found that muscle free from fat and glycogen, and fatigued by work, is richer in nitrogen and slightly so in carbon, but poorer in oxygen. This result has not been published before, methods having to be devised for accurately determining the fat and carbohydrate of muscle; the method now given for the estimation of sugar is a modification of Allihn's. The

main objection to Allihn's method is that asbestos chemically unites with copper, and so some of this metal is lost. The main point about the new method is that the copper is weighed as cuprous oxide after drying on the filter at 120°. W. D. H.

**Diphtheria Antitoxin.** By T. Gregor Brodie (*J. Pathol. and Bacteriol.*, 1897, **4**, 460—464).—These experiments were undertaken with the view of determining the nature of the substance present in the antitoxic diphtheria serum prepared from certain horses, which produces a rash. The results are at present incomplete. It was found that ether, alcohol, acetone, and chloroform extract a substance of an irritating nature from the dried serum; whether this is the material sought for is uncertain. The antitoxic properties of the serum are considerably weakened when redissolved; this is in part due to the process adopted, and the longer the precipitate is left in contact with the precipitant (acetone, or more rapidly with alcohol), the greater is the loss of power due to coagulation of proteid matter. The antitoxin itself is probably proteid in nature; its solubilities are those of a globulin; it will not pass through a gelatin filter, and its power is readily destroyed by dilute alkalis, less readily by dilute acids. W. D. H.

**Ethereal Hydrogen Sulphates in the Urine under the Influence of Drugs.** By Max Mosse (*Zeit. physiol. Chem.*, 1897, **23**, 160).—Dermatol and tannigen have no influence on the excretion of ethereal hydrogen sulphates. Tannalbin increases it; actol diminishes it. In spite of the bactericidal influence of silver chloride in plate cultures, neither it nor argonin lessens the excretion; alcohol also has no effect. W. D. H.

## Chemistry of Vegetable Physiology and Agriculture.

**Carbon Compounds as Food Material for Bacteria.** By Theodor Bokorny (*Pflüger's Archiv*, 1897, **66**, 114—144).—The experiments described in this paper were mostly made with 0·1—0·2 per cent. solutions of different carbon compounds; and mixtures containing several species of bacteria were employed, but they are not specified. Bacteria will grow in solutions of many strong antiseptics of about this strength. The usual mineral salts were also added in each case; the amount of these did not exceed 0·2 per cent. The experiments were carried on at a temperature of 25—30°, and as a rule required 3—6 days, or even longer, before the bacteria grew rapidly.

Methylic alcohol appears to be a fairly good source from which bacteria can obtain their carbon; ethylic and amylic alcohols can also be used. Propylic alcohol serves as a food for fungi, but not for bacteria, whereas benzylic alcohol in 0·1 per cent. solution is a strong poison. Bacteria grow in a 0·08 per cent. solution of phenol, and fungi in a 0·05 per cent. solution. Orthocresol (0·1 per cent.), quinol (0·05), resorcinol (0·05), catechol and phloroglucinol, pyrogallol (0·05), gallic and

tannic acids, will not serve as food material for bacteria; the two latter, however, allow of the growth of fungi. Ethylene glycol, and glycerol are extremely good, whilst tetramethylethylene glycol,

$$OH\cdot CMe_2\cdot CMe_2\cdot OH,$$

is totally useless as food supply.

Different organic acids have also been experimented with, mostly in neutral solutions. There is one species of bacteria which is capable of assimilating formic acid. Acetic, lactic, succinic, tartaric, propionic, aspartic, glyoxylic, pyruvic, levulinic, salicylic, parahydroxybenzoic, and benzoic acids can all be assimilated by bacteria, although benzoic acid acts as a poison to yeast. Oxalic, valeric, citraconic, and mesaconic acids, amido- and nitro-cinnamic acids, cinnamic, hydrocinnamic, and phthalic acids are of no use as food material. Ethylic acetate, ethylic acetoacetate, methylal (1 per cent.), hexamethylenetetramine, acetone, acetaldehyde (0·07 per cent.) can be assimilated, but not glyoxal (0·5 per cent.), paraldehyde, or benzaldehyde. Most carbohydrates, for example, cane-sugar, fructose, *d*-glucose, galactose, milk-sugar, arabinose, sorbose, inosite, mannose, and xylose are extremely good food materials; rhamnose, however, does not act so well. Among cyano- and amido-compounds, acetamide, leucine, methylamine, asparagine, peptone, creatine, and oxamide are extremely useful as sources from which bacteria can obtain their carbon. Nitraniline, anisidine, propylamine, and carbamide are of but little use; whilst ethylenediamine, diacetonamine, trimethylamine, glycocine, potassium thiocyanate, cyanuric acid, and orthotoluidine are quite useless. Anisidine and orthotoluidine can also serve as sources from which the organisms obtain their nitrogen.

J. J. S.

**Alcoholic Fermentation without Yeast Cells.** By EDUARD BUCHNER (*Ber.*, 1897, **30**, 1110—1113. Compare this vol., ii, 154).—The author finds that the aqueous extract loses its fermentative properties when kept for two days at 0°, or for one day at the ordinary temperature. This deterioration of the extract is accompanied by a loss in coagulable albumin, and the deterioration is attributed to the presence of peptonic enzymes. The extract retains its activity much longer in the presence of strong solutions of cane-sugar. When the extract is mixed with its own volume of a 50 per cent. solution of cane-sugar, fermentation continues for 7 days at a moderate temperature, and for 14 days at 0°. That the activity is not due to the presence of plasma particles in the extract is proved by the fact that the activity of the solution is not destroyed by antiseptics, such as chloroform, benzene, sodium arsenite, &c. The extract may also be evaporated to dryness at 30—35° under reduced pressure, and an aqueous solution of the residue is also capable of fermenting cane-sugar. The dried extract may be kept for at least 20 days without losing its active properties. In one instance only was it found possible to precipitate the active substance, *zymase*, by the aid of alcohol.

Well-washed yeast was dried at 37°: one portion, A, was mixed with water and heated to 100°, plate cultures proved that all the cells had been destroyed and yet the solution was capable of fermenting a sterilised cane-sugar solution; the second portion, B, was heated to

140—145° for one hour; this portion, however, was incapable of bringing about fermentation, owing to the destruction of the zymase.

J. J. S.

**The Cause of Poisoning by Wall-papers containing Arsenic.** By B. Gosio (*Ber.*, 1897, **30**, 1024—1026. Compare this vol., ii, 114). *Mucor mucedo*, *Aspergillus glaucus*, and *A. virens* were the first organisms isolated which were capable of decomposing arsenic compounds. The author finds that *Penicillium brevicaule* is also capable of decomposing all solid arsenic compounds, including arsenical dyes; this reaction is so delicate that the author has used it as a means of detecting arsenic. The nature of the volatile arsenical compounds evolved has not been definitely established, although their strongly poisonous character can be readily shown. J. J. S.

**The Cause of Poisoning by Wall-papers containing Arsenic.** By Oskar Emmerling (*Ber.*, 1897, **30**, 1026. Compare previous abstract).—The author states that the volatile arsenical compounds given off by different micro-organisms during the decomposition of solid arsenic compounds is not hydrogen arsenide. Some doubt is also thrown on the poisonous nature of these products. J. J. S.

**Phosphorescence of Wood.** By Fr. Kutscher (*Zeit. physiol. Chem.*, 1897, **23**, 109—113).—Most observers agree that the phosphorescence of decomposing wood is due to fungoid growth. This conclusion has been questioned by De Bary. In the present research, De Bary is shown to be wrong. The fungus was isolated, cultivated on gelatin, and other wood infected with it. Some of the characters of the growth are described, although its place in schemes of classification is not decided. W. D. H.

**Reduction of Nitrates.** By Pierre P. Dehérain (*Ann. Agron.*, 1897, **23**, 49—79).—A number of experiments were made in which solutions of potassium nitrate were inoculated with straw, fresh manure, horse-dung, and peat manure. The results showed the presence of nitrate-reducing organisms in straw and in fresh manure (compare Bréal, Abstr., 1892, 1259; and 1896, ii, 444), but not in peat manure. The horse-dung contained sufficient to reduce nitrates at 30°, but there was very slight reduction at the ordinary temperature.

The denitrifying organisms develop rapidly in solutions containing starch and potassium nitrate: there is no development in pure nitrate solutions. The organisms will live in starch alone, but in absence of nitrate the starch is only very slowly destroyed. Solutions which reduce nitrates most rapidly contain starch (0·25), potassium nitrate, (0·2) and potassium phosphate (0·01 per cent.).

Experiments with soil showed the presence of denitrifying organisms, and that by adding starch a considerable amount of the nitrates present in the soil could be destroyed. The addition of straw containing denitrifying organisms to soil had very little effect on the nitrates present in the soil.

The amount of nitrogen utilised by the reducing organisms is very slight, nearly the whole of the nitric nitrogen being liberated as gas, chiefly free nitrogen. Reduction takes place more readily in closed

vessels than in the open air, and is retarded by passing air through solutions containing starch and potassium nitrate.

There is no danger of loss of nitrogen by the application of the usual amounts of manure. Reduction of nitrates would only take place when the manure amounted to 400,000—800,000 kilos. per hectare. It is, therefore, quite unnecessary to treat stable manure with sulphuric acid before using it. N. H. J. M.

**The Enzyme of Barley which Dissolves Cell-walls.** By FRIEDRICH REINITZER (*Zeit. physiol. Chem.*, 1897, **23**, 175—208).—The author failed to obtain cytase, the cell-dissolving enzyme of barley described by Brown and Morris (Trans., 1890, 497). The diastase of germinating barley has, however, the power of dissolving the readily hydrolysible hemicelluloses, which probably have a very widespread distribution in the vegetable kingdom; but many of the hemicelluloses are not attacked by diastase. When these pass into solution as germination proceeds, no doubt some ferment which may be called cytase is at work. W. D. H.

**Composition and Analysis of Wheat.** By AIMÉ GIRARD (*Compt. rend.*, 1897, **124**, 876—882).—In order to be of value for manufacturing purposes, chemical analyses of wheat should be made, not on the whole grain, but on the products of a mechanical analysis, corresponding as closely as possible with the operations of milling. Two analyses, one of the usable flour, the other of the bye-products, are generally sufficient. On mechanical analysis, four French wheats of 1895 gave: water 14·50 to 15·12, kernel 83·04 to 85·98, germ 1·16 to 1·50, envelope 12·52 to 15·61 = 100. The average weight of a grain was 0·038 to 0·051 gram.

Of substances soluble in water, the proportion in flour is generally given as 10 to 12 per cent. of the weight of the wheat, and they are said to consist of about 50 per cent. of glucose and dextrin. These results are, however, erroneous, and are due to the action of the diastases in the wheat during the somewhat long soaking in water which is generally given for the purpose of extracting the soluble matter. Accurate estimations are obtained by agitating the flour with ice-cold water for about 4 hours; the proportion of soluble matter does not exceed 4 or 5 per cent. and it contains a very small quantity of glucose and no dextrin. It is only by the use of a low temperature that the action of the diastases can be minimised; such antiseptics as could be used are without effect.

When the aqueous solution at 0° is mixed with four times its volume of alcohol of 95° a white, flocculent precipitate is formed, which contains no dextrin but consists of nitrogen compounds (including diastases) together with about 1 per cent. of galactin, the gum corresponding with galactose and described by Müntz. The alcoholic liquid contains no dextrose, but from 1 to 2 per cent. of saccharose.

The ordinary method of estimating gluten is the simplest and most accurate, but it is important that it should be dried at 100—105°, and the drying is facilitated by first coagulating the gluten by immersing it for a few minutes in boiling water. The proportion of glutenin and gliadin in the gluten should be estimated by Fleurent's method (*Compt. rend.*, **123**, 327), since when the ratio differs much from 25 per cent. of

the former, to 75 per cent. of the latter, the flour does not yield bread of such good quality.

Starch is generally estimated by difference or more rarely by conversion into sugar, but direct estimation by washing, collecting on a very fine sieve and drying at 100—105°, is simpler and at least as accurate. For the estimation of fat, crystallisable benzene is preferable to ether.

Analyses of the four French wheats previously referred to gave the following results: Water 14·74 to 15·58; matter soluble in water 3·12 to 4·00 per cent., consisting of glucose 0·09 to 0·21, saccharose 0·86 to 1·70, nitrogen compounds 1·02 to 1·28, galactin, &c., 0·52 to 0·99, inorganic matter 0·22 to 0·36; matter insoluble in water 79·94 to 80·94 per cent., consisting of gluten 7·45 to 8·32, starch 69·88 to 71·22, fat 0·84 to 1·12, inorganic matter 0·20 to 0·40, cellular matter and dèbris 0·22 to 0·25; acidity in terms of sulphuric acid 0·006 to 0·011. The ratio of glutenin to gliadin varied from 25/62 to 25/87. C. H. B.

**Manure Value of Oil Cakes.** By L. MALPEAUX (*Ann. Agron.*, 1897, **23**, 28—42).—Field experiments were made in which barley and sugar-beet were grown without manure, with sodium nitrate (300 kilos. per hectare), and with nine different kinds of oil cake (1000 kilos. per hectare). In a second series, superphosphate was applied in addition to the nitrogenous manures, and also to a plot not otherwise manured. Two similar series of pot experiments were also made.

The effect produced by the cakes is chiefly due to the nitrogen they contain. The different cakes vary considerably in value. The use of superphosphate in addition to cake is not necessary when the soil contains over 0·1 per cent. of phosphoric acid. The best time for applying cake is the autumn; when applied in the spring, the results are uncertain, being dependent on climatic conditions. Of the different cakes employed, sesame cake was the most effective: earth nut cake was less favourable, rape cake, cotton cake, and castor-oil cake still less so. This scale of value is, however, not absolute, being based on only one year's results. N. H. J. M.

**Bat Guano from Eboli, Salerno.** By JULES PARIS (*Ann. Agron.*, 1897, **23**, 47—48).—The sample analysed contained: water 18·02, mineral matter 52·87, and nitrogen (almost entirely as nitrates) 2·996 per cent. The ash, of which 25·61 per cent. was soluble, had the following percentage composition:—

| $K_2O$. | $Na_2O$. | CaO. | MgO. | $Al_2O_3$ & $Fe_2O_3$. | $P_2O_5$. | Insol. in HCl. |
|---|---|---|---|---|---|---|
| 2·08 | 0·81 | 13-84 | 0·18 | 16·85 | 20·69 | 44·69 |

Of the phosphoric acid, 47·96 per cent. was soluble in ammonium citrate. The ash contained a small amount of copper, and traces of manganese. It is suggested that the presence of copper is due to the bats having eaten insects containing copper (compare Giunti, *Ricerche sulla Diffusione del Rame*, Naples, 1881.) N. H. J. M.

## Analytical Chemistry.

**Apparatus for Gas Analysis.** By OTTO BLEIER (*Ber.*, 1897, 30, 1210—1211. Compare Abstr., 1896, ii, 70; this vol., ii, 280).—The author has improved the gas burette which he formerly described by replacing the upper tap by a three way tap, so that gas can be transferred from the pipette to the burette without either loss or addition.

A. H.

**Preparation of Reagents Free from Arsenic.** By JOSEF HABERMANN (*Zeit. angw. Chem.*, 1897, 201—202).—Hydrochloric acid is mixed with a little potassium chlorate (0·5 gram per litre is generally sufficient), and the liquid distilled and condensed in a receiver containing an appropriate amount of water; the distillation is stopped when about 75 per cent. of the acid has distilled over. All the arsenic remains in the retort, and the distillate will not contain a trace of it; it contains a small amount of free chlorine, however, which in toxicological investigations is of no consequence.

Ammonia, free from arsenic, may be obtained by adding to the commercial article a little potassium permanganate, heating the mixture in a flask and passing the gas into distilled water.

Ammonium sulphide, free from arsenic, is obtained by passing hydrogen sulphide into the purified ammonia. To obtain the hydrogen sulphide free from arsenic, the excess of moisture is removed, and the gas is then passed first through a tube containing a small quantity of iodine and subsequently through a wash bottle containing water.

L. DE K.

**A Simple Method of Quantitative Analysis by Means of the Telephone.** By HUGO ERDMANN (*Ber.*, 1897, 30, 1175—1182). —The solubility of sparingly soluble substances has been determined from the electric conductivity of the saturated solutions (Kohlrausch and Rose, Abstr., 1894, ii, 7), and the same property has been utilised by Beckmann to evaluate milk, wine, and beer. Taking advantage of the considerable differences in conductivity exhibited by solutions of potassium chloride, bromide, and iodide, the author has elaborated a method by which mixtures of these electrolytes may be analysed quantitatively by means of the wire-bridge and telephone.

To the extremities of the wire, which are placed in connection through an induction apparatus situated in a neighbouring room, are connected two Arrhenius' resistance cylinders $W$ and $W'$, with the junction of which the sliding-piece communicates through a telephone; in order to eliminate the effect on conductivity produced by temperature, both cylinders are placed in the same vessel containing water. If now a mixture of potassium chloride and bromide is to be analysed, the cylinders are filled with a 1 per cent. solution of the former salt, and the position of minimum disturbance recorded; $W'$ is then refilled with a 1 per cent. solution of potassium bromide, and a fresh observation made. The mixture of unknown composition is afterwards in-

troduced into $W'$, in the form of a 1 per cent. solution, when its conductivity may be compared with that of the pure potassium chloride; the ratio of the resistance of the latter to the resistance of the mixture decreases as the percentage of potassium bromide in the mixture is increased, and the decrease being directly proportional to the rise in percentage of potassium bromide, the amount of the latter salt which is present in the mixture may be calculated.

This method of analysis has been applied to mixtures of potassium chloride with potassium bromide, potassium bromide with potassium iodide, and potassium chloride with potassium iodide, and also to a mixture of potassium sulphate with rubidium sulphate. M. O. F.

**Separation of Chlorine and Bromine.** By HENRI BAUBIGNY and PAUL RIVALS (*Compt. rend.*, 1897, **124**, 859—862).—It is well known that potassium permanganate does not decompose alkali bromides or chlorides in aqueous solution. If, however, the alkalis are displaced by some other metals, decomposition may take place. Cupric bromide is decomposed by the permanganate at the ordinary temperature with liberation of bromine, but cupric chloride is not affected. In order to separate the two halogens in this way, the carefully neutralised solution of chloride and bromide is mixed with excess of cupric sulphate, and potassium permanganate is added and the liquid allowed to evaporate in a vacuum over potassium hydroxide at the ordinary temperature. A large, flat dish should be used, so that the residual salt forms only a thin film in which very little bromine can be occluded. If necessary, the residue may be moistened with water and again allowed to evaporate under the same conditions. The chlorine is precipitated with silver nitrate containing a considerable proportion of nitric acid, after the permanganate has been reduced with sulphurous acid.

If aluminium sulphate is substituted for cupric sulphate, there is considerable loss of chlorine under the same conditions. C. H. B.

**Study of Kjeldahl's Process and its Modifications.** By G RIVIÈRE and G. BAILHACHE (*Bull. Soc. Chim.*, 1897, [iii], **15**, 806—811).—The authors employ sodium pyrophosphate in place of the potassium sulphate generally used. A table showing the time occupied by the analysis, and the results obtained by different methods, is given.

M. W. T.

**Colorimetric Estimation of Nitrous Acid.** By E. RIEGLER (*Zeit. anal. Chem.*, 1897, **36**, 306—307).—A typical solution is prepared by dissolving 0·406 gram of silver nitrite in hot water, adding a small excess of sodium chloride, and diluting to a litre. Of the clear solution, 100 c.c. is again diluted to a litre, and 100 c.c. of this dilution (corresponding with 0·001 gram of $N_2O_3$) is mixed in a flask with about 0·05 gram of crystallised naphthionic acid, 5—6 drops of concentrated hydrochloric acid, and, after thorough shaking, 30 drops of strong ammonia. The solution to be assayed is treated in like manner, and the rose-red colours compared in a colorimeter. 0·00001 gram of $N_2O_3$ in 100 c.c. can be estimated by this method. M. J. S.

**Estimation of Carbon in Ferro-Chrome.** By HARRY BREARLEY and RUDOLF L. LEFFLER (*Chem. News*, 1897, **75**, 241—243).—The pulverised ferro-chrome is mixed with pulverised lead chromate, placed in a boat, and burnt in a current of oxygen in a tube packed with copper oxide; the reaction in the boat, which has to be assisted by heating with a foot blowpipe, takes place with great rapidity at one stage and is sluggish at another; therefore a reservoir is interposed, at the oxygen supply end, to accommodate the rush of gas and to subsequently permit of its steady passage through the tube; moreover, the tube is protected against the great heat by wrapping it first with paper and then with asbestos millboard, the paper leaving a layer of ash that prevents the asbestos fusing to the glass; millboard is also used to prevent the porcelain boat employed from fusing to the tube. Zinc oxide and litharge used instead of lead chromate did not give satisfaction; with copper oxide, the heat has to be greater and the reaction is less violent; but lead dioxide is effective and convenient, for it does not require the aid of a blowpipe flame. D. A. L.

**Solubility of Potassium Platinochloride in Alcohol.** By M. PÉLIGOT (*Zeit. anal. Chem.*, 1897, **36**, 322; from *Mon. sci.*, [iv], **6**, 872).—One litre of alcohol at 20° dissolves the following amounts of potassium platinochloride:

| | | | |
|---|---|---|---|
| Strength of alcohol | 85 | 90 | 95 per cent. |
| Potassium platinochloride dissolved | 0·180 | 0·100 | 0·030 gram. |

A mixture of 800 c.c. of 95 per cent. alcohol and 200 c.c. of ether dissolves 0·027 gram. These corrections are not applicable to potassium estimations, since the solubility is modified by the presence of sodium platinochloride. M. J. S.

**Estimation of Potassium.** By HENRY N. WARREN (*Chem. News*, 1897, **75**, 256).—The solution of the alkali chlorides is heated and evaporated to a small bulk with excess of platinic chloride, and then mixed with double the original quantity of a mixture of amylic alcohol and ether in equal proportions. The precipitate is washed with the same mixture, heated to the boiling point with formic acid, and the precipitated platinum washed, dried, and weighed; the percentage of potassium is calculated from this weight. D. A. L.

**Testing Sodium Hydrogen Carbonate.** By GEORGE LUNGE (*Zeit. angw. Chem.*, 1897, 169—171).—The author communicates a process originated by Sundstrom, and thinks that it may be recommended. The sample is dissolved in cold water and titrated with standard soda, which has been nearly saturated with baryta (so as to be perfectly free from carbonate), until a drop of the liquid gives a brown coloration with silver nitrate. From the results, the excess of carbonic acid present above that required for the normal carbonate can easily be calculated.

Another portion of the sample is then titrated with standard acid, using methyl-orange as indicator. We have then the means for calculating the purity of the salt. L. DE K.

**Estimation of Zinc Oxide.** By EMILY ASTON and L. NEWTON (*Chem. News*, 1897, **75**, 133—134).—Fresenius states that zinc oxide

when mixed with sulphur, and gradually heated to redness in a current of hydrogen is quantitatively transformed into zinc sulphide. The authors find this to be the case with zinc oxide prepared by ignition from the carbonate, sulphide or sulphate; but with oxide prepared from the nitrate, in the manner set forth below, the result falls short of the theoretical by some 10 per cent., a number that is reduced by very small quantities at a time by repeating the operation, which, in one case, was done above 22 times; but even then the quantity of zinc sulphide did not exceed 96 per cent. of the theoretical. The oxide, that behaved in this manner, was prepared by dissolving practically pure zinc in pure nitric acid, evaporating the solution to dryness, dissolving the residue in water, filtering the solution, treating the filtrate with a few drops of ammonium sulphide, agitating frequently, and again filtering. This solution was then evaporated to dryness, the residue dried at 150°, and ignited first in a blowpipe and then in a muffle.

D. A. L.

**Estimation of Manganese in Manganous and Permanganic Solutions.** By ANTONIO LONGI and S. CAMILLA (*Gazzetta*, 1897, **27**, i, 97—117).—The authors have re-investigated Volhard's modification (Abstr., 1880, 141) of Gensard's method (*Bull. Soc. Chim.*, [ii], 1, 88) of estimating manganese in a manganous solution by titrating it with potassium permanganate, when the following reaction occurs: $3MnO + Mn_2O_7 = 5MnO_2$; addition of nitric acid to the solution, as recommended by Volhard, does not clarify it successfully, but this object may be attained by titrating in a solution containing about 0·025 per cent. of manganese and 0·5 per cent. of zinc sulphate. Meinecke's criticisms (*Rep. Anal. Chem.*, 1885, **5**, 1) of Volhard's method are mostly unfounded. The manganous solution containing zinc sulphate is titrated at the boiling temperature with N/10 potassium permanganate solution until a persistent red colour is obtained; the precipitate should settle readily, leaving the supernatant liquid clear. Any adherence of manganese dioxide to the sides of the flask is due to the latter being dirty, and may be prevented by previously washing with a sulphuric acid solution of chromic anhydride. After cooling the titrated solution, a check on the result is obtained by adding potassium iodide and hydrochloric acid, and titrating the liberated iodine with thiosulphate; this is the more necessary when much chromium salts are present, since these obscure the end reaction with permanganate, and in such a case it is advisable to filter off the manganese dioxide through a filter paper before treating it with potassium iodide.

Permanganates may be determined by titration with a manganous salt in neutral solution, or in one slightly acidified with acetic or nitric acid. The estimations may be performed in presence of chromic acid, nickel, cobalt, and lead.

W. J. P.

**Separation of Nickel from Cobalt and Iron, and of Cobalt from Aluminium.** By EUGENIO PIÑERÚA (*Compt. rend.*, 1897, **124**, 862—863).—Nickel chloride is insoluble at a low temperature in ether saturated with hydrogen chloride, whereas cobalt and ferric chlorides dissolve readily. In order to utilise these facts for analytical purposes, the metals are converted into chlorides, which are dissolved

in the smallest possible quantity of water, a moderately large quantity of a mixture of equal volumes of concentrated hydrochloric acid, and ordinary, or preferably dry, ether is added, and a current of hydrogen chloride is passed into the liquid, which is cooled in a mixture of ice and salt. The yellow precipitate of nickel chloride is washed with ether saturated with hydrogen chloride, at first by decantation and afterwards on a filter.

The so-called pure compounds of nickel and cobalt are generally more or less impure; the former contain cobalt and iron, and the latter contain nickel and iron.

When applying this method to the separation of nickel from iron, the precipitate must be very well washed, redissolved in water, and the operation repeated several times in order to eliminate the iron which the nickel chloride obstinately retains.

Cobalt can be separated from aluminium in the same way, the aluminium chloride being precipitated. C. H. B.

**Separations with Alkali Acetates.** By HARRY BREARLEY (*Chem. News*, 1897, **75**, 253—254).—The author shows that the quantity of sodium or ammonium acetate required to completely precipitate the iron from "neutralised" solutions of ferric chloride (that is, solutions of ferric hydroxide in ferric chloride) is diminished by the proportion of hydroxide, and increased by the amount of free acetic acid in solution. Incidentally, it is observed that small quantities of iron may be removed from solutions by an asbestos filter, and that salts of the alkalis exert to a certain extent a neutralising effect, the chlorides being more active than the nitrates in this respect. D. A. L.

**Estimation of Titanic Acid.** By J. JAMES MORGAN (*Chem. News*, 1897, **75**, 134).—The author approves of the following combination of the methods of Arnold and of Blair. The ore, mixed with 1 gram of ammonium phosphate in solution in a small quantity of water, is dissolved in hydrochloric acid, and the solution evaporated to dryness. The residue is well dried ("well baked"), extracted with hydrochloric acid, the solution diluted, and the residue, which contains all the titanic acid as phosphotitanate of iron, is collected, washed free from iron salts with hot dilute hydrochloric acid and cold water, and after drying is fused in a platinum crucible with ten times its weight of potassium carbonate. The mass is treated, and washed carefully, with hot water, and the dried residue is fused in a platinum crucible, at a low red heat, for half an hour with about 6 grams of potassium hydrogen sulphate. When cold, the mass is treated with 10 c.c. of hydrochloric acid and 50 c.c. of sulphurous acid, filtered, and washed with hot water; 20 grams of sodium acetate in aqueous solution is added to the solution, which is then boiled for a few minutes with one-sixth of its volume of acetic acid; the precipitate is washed, dried, ignited, and weighed as $TiO_2$.

Pig iron, without addition of ammonium phosphate when the phosphorus is high and the titanium low, is dissolved in nitric acid (sp. gr. = 1·20), and the solution evaporated to dryness; the residue is then thoroughly dried, dissolved in hydrochloric acid, and the drying repeated; finally, the mass is again dissolved in hydrochloric acid, and the solution diluted, filtered and treated as above. D. A. L.

# General and Physical Chemistry.

**Absorption Spectra of some Compounds in the Gaseous and Liquid States.** By J. PAUER (*Chem. Centr.*, 1896, i, 1122; from *Ber. Physikal.-Med. Soc. Erlangen*, 27, 120—126).—The substances examined were benzene, toluene, the xylenes, ethylbenzene, chloro-, bromo-, iodo-, nitro-, amido-, azo-, and amidoazo-benzene; carbon bisulphide, pyridine, thiophen, anthracene, and naphthalene. Their absorption spectra are in the ultra-violet, and were therefore in each case photographed. All the compounds in the liquid state, or in solutions of suitable concentration, give rise to absorption bands near the cadmium lines 17—20 (Mascart's definition). The absorption spectra of the same substance in solution in different solvents show a displacement towards the red which increases with the refractive index or the dispersion of the solvent. The absorption spectra of the vapours consist of lines, or groups of lines, which form one or more bands as the substance passes from the gaseous to the liquid state. The position of the bands for the liquid is always nearer the red than that of the lines or groups of lines, for the vapour.

The influence of constitution on the absorption in the case of the benzene derivatives was not found to follow any regular course. The character of the absorption alters entirely with the substitution of different hydrogen atoms. Nitrobenzene and iodobenzene in the gaseous state give rise to no lines whatever. Benzene, naphthalene, and anthracene in solution each give four bands, which lie nearer to the red the greater the molecular weight of the compound. The substitution of N for CH entirely alters the character of the benzene spectrum. The absorption in the case of benzene and anthracene is very intense, so that even traces of the vapour of the former in admixture with air could be detected. H. C.

**Internal Resistance of Galvanic Cells.** By ERNST HAAGN (*Zeit. physikal. Chem.*, 1897, 23, 97—122).—The author describes a method for the determination of the internal resistance of cells which is fundamentally similar to the Wheatstone bridge method for the comparison of the capacities of condensers, the known ratio of the capacities giving the ratio of the resistances. The availability of the method for various classes of cells is first proved by comparison of the results obtained with those obtained by other methods. The experiments afterwards show that the internal resistance of cells during electrolysis is quite independent of the current strength or current density. The slight variations which were found to occur are traceable to alterations in the concentration of the solutions. In the case of accumulators, during discharge the resistance at first slowly increases, the rate of increase being more rapid towards the end; whilst during the charging of the cell the reverse changes occur, the resistance at first diminishing rapidly and afterwards more slowly. The cause of this variation is partly the

change in concentration of the sulphuric acid, and partly alteration of the surface of the lead plates. L. M. J.

**Theory of Lead Accumulators.** By C. Liebenoff (*Chem. Centr.*, 1896, ii, 409; from *Zeit. Electrotechn. und Electrochem.*, 1896, 2, 653—655).—Experiments have been made by the author with the object of proving the existence of lead dioxide in the ionic condition, as required by his theory of lead accumulators (this vol., ii, 239). In a vessel which contained a normal solution of a caustic alkali saturated with lead oxide, three cylinders, the lower ends of which were closed membranes, were placed, and these were filled with normal alkali to the level of the solution in the containing vessel. Electrodes were placed in the first and third cylinders, the centre one serving for the estimation of the lead entering the cylinders by diffusion. After a current had been passed for some time, lead was found in quantity round the positive electrode, but was practically absent at the negative electrode. The compound $Pb(OK)_2$ gives, therefore, the ions $2\overset{+}{K}$ and $\overset{--}{PbO_2}$. This result was confirmed by other experiments. H. C.

**Electrolytic Decomposition of Aqueous Solutions.** By Walther Nernst (*Ber.*, 1897, 30, 1547—1563).—In a lecture before the German Chemical Society, the author reviews the present position of the question of the chemical mechanism of the electrolytic decomposition of aqueous solutions. The author's method (Abstr., 1889, 1095) of calculating the potential difference between a metal and a solution, from the solution pressure of the metal and the osmotic pressure of the solution, is first described, and it is pointed out that the E.M.F. of the galvanic cell formed by combination of two different electrodes is thus readily obtained. By what is practically a reversal of this process, Le Blanc (Abstr., 1891, 1405) obtains the minimum value of the E.M.F. necessary to produce sensible electrolysis in any given solution. The want of agreement between the numbers obtained in practice and those which the theory would predict in certain cases, leads Le Blanc to the view that water sometimes plays a primary part in electrolysis, and is directly decomposed by the current. The E.M.F. necessary to effect this result is according to Le Blanc's measurements 1·68 volt., but from Smale's work on gas batteries (Abstr., 1894, ii, 436) the maximum value should be 1·08 volt. From measurements made in the author's laboratory by Glaser, it appears that a primary decomposition of water can be effected in the case of sulphuric acid and potassium hydroxide solutions with an E.M.F. of 1·08 volts., if the oxygen separates on a large platinised electrode. The point 1·68 volt. is in these cases, however, also characterised by some further decomposition in the solutions. The suggestion is made that water not only dissociates into the ions OH and H, but also into H, H and O, and that the lower E.M.F. is that under which separation of the latter ions takes place, whilst the higher E.M.F. gives rise to separation of the hydroxyl and hydrogen ions.

In the following table, the pressures (in volts.) required for the separation of certain cations and anions from solutions of normal concentration are given:

| Cations. | | Anions. | |
|---|---|---|---|
| Ag | −0·78 | I | 0·52 |
| Cu | −0·34 | Br | 0·94 |
| H | 0·0 | O | 1·08 |
| Pb | +0·17 | Cl | 1·31 |
| Cd | +0·38 | OH | 1·68 |
| Zn | +0·74 | $SO_4$ | 1·9 |
| | | $HSO_4$ | 2·6 |

The hydrogen value is taken as zero, as it is evident that an arbitrary value has to be assigned to one of the terms. From this table it is possible to calculate the E.M.F. required for the electrolysis of normal solutions of salts of any of these ions; for zinc bromide, for instance, we get $0·74 + 0·94 = 1·68$ volt. It is further evident that these values indicate the possibility of separating certain ions electrolytically, as has been done by Freudenberg (Abstr., 1893, ii, 506). A large number of other conclusions with reference to chemical action in solution may be drawn from this table, as, for example, for the displacement of one ion by another. It must, however, be remembered that the pressures form only one factor in such changes, and that ionic concentration must also be taken into consideration. H. C.

**Determination of Osmotic Pressure by Means of Vapour Pressure Measurements.** By ARTHUR A. NOYES and CHARLES G. ABBOT (*Zeit. physikal. Chem.*, 1897, **23**, 56—77).—By observations of the vapour pressure of a solution, the osmotic work is directly obtained. The authors deduce an expression for the osmotic pressure. $P = (1 + \frac{P}{2}k)\frac{s_0}{M}\int_p^{p_0} vdp - (p_0 - p)$ where $P$ is osmotic pressure and $p$ the vapour pressure of the solution; $p_0$ is the vapour pressure, $s_0$ the density, $v$ the gaseous molecular volume, $M$ molecular weight, and $k$ compressibility of the solvent. This expression, by neglecting the small terms $\frac{P}{2}k$ and $p_0 - p$ reduces to $P = \frac{s_0}{M}\int_p^{p_0} vdp$, and gives for the osmotic work $\pi = Pv_0/(1 + \frac{P}{2}k)$ where $v_0$ is molecular volume of the solvent. As $k$ is very small, the osmotic work is hence approximately proportional to the osmotic pressure, and relations deduced from the former hold also for the latter. The authors then describe a series of very careful determinations of the osmotic pressure in the case of ethereal solutions of naphthalene and azobenzene. The vapour pressure of the solution was determined by the dynamical method, the liquid being kept boiling at a temperature of 12·9°, a form of electrical resistance thermometer being employed. The vapour pressure of the pure ether was obtained from Ramsay and Young's numbers (*Phil. Trans.*, 1887, **178**, 63), the physical constants of the liquid employed agreeing exceeding closely with those given by Ramsay. The values for the osmotic pressure and the product, (pressure) × (volume of solutions containing the gram molecular weight) is given in the accompanying table.

| Concentration. | P. (naphthalen). | Pv. | P. azobenzene. | Pv. |
|---|---|---|---|---|
| 0·01 | 1·562 | 27·93 | 0·958 | 24·35 |
| 0·02 | 2·942 | 26·46 | 1·900 | 24·29 |
| 0·03 | 4·293 | 25·91 | 2·773 | 23·77 |
| 0·05 | 6·875 | 25·21 | 4·620 | 24·04 |
| 0·07 | 9·357 | 24·83 | 6·349 | 23·87 |
| 0·10 | 12·87 | 24·35 | 8·858 | 23·73 |
| 0·13 | 16·27 | 24·11 | 11·28 | 23·64 |
| 0·16 | 19·55 | 23·94 | 13·66 | 23·66 |
| 0·20 | 23·79 | 23·84 | 16·71 | 23·69 |
| 0·24 | 27·80 | 23·73 | 19·62 | 23·67 |

It is clear that the values agree very closely with those of a perfect gas at equal concentrations; the gas constant for hydrogen at 12·9 being 24·27, and the van't Hoff law regarding the equality of pressures in the gaseous state and solution is found valid for both compounds. L. M. J.

**Saturated Solution of Magnesium Chloride and Potassium Sulphate, or of Magnesium Sulphate and Potassium Chloride.** By RICHARD LÖWENHERZ (*Zeit. physikal. Chem.*, 1897, **23**, 95—96).—The composition of the solutions of the above salts at 25°, previously given by the author (Abstr., 1894, ii, 273), was incorrect, owing to the fact that the solutions were not previously heated above this temperature and allowed to cool, a precaution necessary owing to the slight solubility of the potassium salt in the magnesium solution (Abstr., 1894, ii, 273). L. M. J.

**Study of Water Solutions of some of the Alums.** By HARRY C. JONES and E. MACKAY (*Amer. Chem. J.*, 1897, **19**, 83—118).—The alums, in dilute solution, have a conductivity which is almost exactly the mean of the conductivities of their constituents, from which it follows that the complex alum molecules are broken down completely in such solutions into the molecules of the simpler sulphates, and that these simpler molecules dissociate as if alone, barring the effect on the dissociation produced when the solutions are not isohydric. In concentrated solutions, the alums show a conductivity less than the mean of the conductivities of their constituents. The difference becomes more marked as the concentration increases, and is of the same order as that observed for other double sulphates. It is much greater than that found in the case of mixtures of sulphates incapable of yielding a double salt. This must be regarded as evidence that the alums are partially undecomposed into the constituent molecules in such solutions, or that the dissociation into the simple ions into which the single sulphates break down is not complete. The magnitude of the difference for potassium chromium alum, as compared with the aluminium alums, affords strong evidence that this alum at least exists as such in moderately concentrated solutions. The freezing point determinations confirm the evidence from the conductivity, that the alum molecules exist to some extent in the more concentrated solutions. H. C.

**Use of the Mass-action Law in the Examination of Organic Additive Products. The Reaction between Picric Acid and β-Naphthol in Aqueous Solution.** By BASIL B. KURILOFF (*Zeit. physikal. Chem.*, 1897, **23**, 90—94).—If to a saturated solution of β-naphthol, picric acid is added, the solubility of the former increases owing to the formation of an additive product of the two compounds. Hence, if the solubility of the β-naphthol is represented by $a$ in gram-molecules, and by $c$ after addition of $b$ gram-molecules of picric acid, then $c-a=$ the number of gram-molecules of the β-naphthol picrate and $b-(c-a)$ the number of free molecules of picric acid, so that the equilibrium constant is hence given by the equation $k(c-a)=a(b-c+a)$. The estimation of the β-naphthol was made by the method indicated by Küster (Abstr., 1894, ii, 432), and although the picric acid was found to interfere with the estimation, this was avoided by the use of a suitable quantity of sodium hydroxide. The values then calculated from different experiments for $k$ gave very fair agreement, that is, within about 10 per cent. of the mean.

The results were calculated without regard to differences in dissociation of the naphthol picrate and picric acid; that is, on the assumption that they are equally dissociated, this being shown to be valid by conductivity determinations. L. M. J.

**The Transition of Seignette Salt and of the Corresponding Ammonium Compound.** By J. DOCTERS VAN LEEUWEN (*Zeit. physikal. Chem.*, 1897, **23**, 33—55).—The transition temperatures of sodium and potassium racemates and of Scacchis salt had been previously determined (Abstr., 1895, ii, 380 and 485), and the author therefore extended these observations to the sodium potassium and sodium ammonium tartrates. Rochelle salt, on evaporation, first deposits sodium tartrate, indicating a decomposition into the sodium and potassium compounds. The transition temperature for this change was determined for the dry salt by the dilatometric method, and found to be about 55°, the change being represented by the equation $2NaKC_4H_4O_6,4H_2O \gtrsim 0{\cdot}54Na_2C_4H_4O_6,2H_2O + 0{\cdot}20K_2C_4H_4O_6,\frac{1}{2}H_2O + 6{\cdot}8H_2O$; $0{\cdot}46Na_2C_4H_4O_6$; $0{\cdot}80K_2C_4H_4O_6$ (saturated solution). The experimental numbers and diagrams are given for the solubility relations in the case of solutions of Rochelle salt, mixed tartrates, Rochelle salt and potassium tartrate: Rochelle salt and sodium tartrate.

In the latter case, at temperatures above 40°, the number of molecules of dissolved potassium tartrate exceeded that of sodium tartrate, indicating the splitting-up of the Rochelle salt. Above 40°, therefore, a saturated solution of Rochelle salt deposits crystals of a mixture of the salt with sodium tartrate, and above 55°, a mixture of the two simple tartrates. With sodium ammonium tartrate, the decomposition takes place according to the equation

$$2NaNH_4C_4H_4O_6,4H_2O \gtrsim Na_2C_4H_4O_6,2H_2O + (NH_4)_2C_4H_4O_6 + 6H_2O,$$

the transition temperature as obtained by both dilatometric and tensimetric methods being about 58·5—59°. By measurement of the ratios of the vapour tension of the salt to that of water at different temperatures, the heat of combination with water is obtained by the expression $q=2T_1T_2/(T_1-T_2)\cdot\log F_1/F_2$ where $F_1$ and $F_2$ are the above ratios at

the absolute temperatures $T_1$ and $T_2$. In the case of Rochelle salt, the values so obtained vary from 2245 to 2527 Cal. (18—31°), and agree well with the value 2373 calculated from the known heats of solution of the tartrates. During the work, the author obtained sodium tartrate with $2H_2O$, in the form of a hard, glassy mass melting at 60°.

L. M. J.

**Influence of Pressure on the Velocity of Reactions in Homogeneous Fluid Systems.** By A. BOGOJAWLENSKY and GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1897, **23**, 13—23).—The effect of pressure on the velocity of a reaction is given by the expression $\frac{dk}{dp} = \gamma\left(m'_2 \frac{dm'}{dp} + m'_1 \frac{dm'_2}{dp}\right)$ where $m'_1$ and $m'_2$ are the active masses of the reacting compounds. The alteration of the active mass may be calculated in the case of electrolytes; for non-electrolytes, the influence of pressure on the active mass is proportional to the concentration of the compound. It hence follows that, in reactions between strongly dissociated compounds and non-electrolytes, the percentage pressure change of velocity is independent of the concentration of the electrolyte; Stern (this vol., ii, 92) found the velocity increased slightly with the concentration.

By variation of the non-electrolyte, the influence of pressure on the absolute velocity is proportional to the concentration. Its influence hence on the velocity constant is independent of the concentration results in accord with the experiments of Stern. As the volume change decreases up to 50° in aqueous solutions, the temperature coefficient of the pressure change is negative for aqueous solutions, but may be positive or negative with other solvents, a result in accord with Stern's experiments. The effect also varies with the nature of the electrolyte. Thus the increase of velocity by a pressure of 500 atmospheres is 14 per cent. higher in the case of the hydrolysis of methylic acetate by acetic acid than the case of the similar reaction with hydrochloric acid, the increase in dissociation being 9 per cent. greater. The pressure effect for weak bases was also studied by means of the hydrolysis of methylic acetate by ammonium hydroxide, the velocity being doubled by a pressure of about 2000 atmospheres. The effect on weak bases and acids is hence greater than on the stronger compounds, but the pressure at which equal velocities would obtain is too high to be calculated by extrapolation.

L. M. J.

**Velocity of the Hydrolytic Decomposition of Carbonyl Sulphide.** By GUSTAV BUCHBÖCK (*Zeit. physikal. Chem.*, 1897, **23**, 123—156).—Carbonyl sulphide decomposes in the presence of water with the formation of carbonic anhydride and hydrogen sulphide, $COS + H_2O = CO_2 + H_2S$, and the author endeavoured to investigate the velocity of the reaction and the effect of various chemically inactive compounds. The extent of the decomposition was determined by the addition of iodine and titration of the excess by sodium thiosulphate; that of the total sulphide by decomposition by alkali, acidification and subsequent iodine titration. For an irreversible reaction, the equation $\frac{dx}{dt} = k(C-x)(A-x)$ should obtain where $x$ is the concentration of de-

composed sulphide and $C$ and $A$ that of undecomposed sulphide and water respectively, this reducing with excess of water to $dx/dt = K(A-x)$. The first set of experiments on the velocity of decomposition by means of water gave a constant value for $K$, so that the reverse action does not obtain, neither have the products any influence on the velocity. The velocity of decomposition in the presence of acids was next determined, and it was found that the velocity decreases on the additions of acids, the decrease being greater for the more highly dissociated acids, and increasing with the concentration. Monochloracetic acid, however, caused a very slight increase of velocity, and metallic salts in many cases also cause an increase. For a series of allied salts the velocity increases with the atomic weight of the metal, so that it appears as a periodic function of the atomic weight, and may be approximately calculated as an additive function of the anion and cation. The author suggests that the decomposition may be represented by $COS + \overset{+}{H} + \overset{-}{O}H \leftrightarrows SH \cdot CO \cdot OH$ and then $SH \cdot CO \cdot OH = H_2S + CO_2$, in which the quantity of the thiocarbonic acid is always proportional to the carbonyl sulphide, so that the alterations of velocity are those of the second reaction. The effect of the salts on the velocity and their internal friction were compared, and although for the metallic salts a parallelism appears to exist, this breaks down if the acids are included.

The effects of carbamide and glycerol were also determined, both compounds causing an acceleration.

The effect of temperature was also investigated, and found to be well represented by the van't Hoff equation, $\log K = B - A/T$ where $T$ is the absolute temperature and $A$ and $B$ are constants. L. M. J.

**Study of Atomic Weights.** By JOHANNES R. RYDBERG (*Zeit. anorg. Chem.*, 1897, 14, 66—102).—The author regards the atomic weights of the elements as forming a discontinuous series of numbers, which are not multiples of the atomic weight of hydrogen, although in the case of those elements which have a lower atomic weight than 56, this condition is more nearly fulfilled than could be accounted for by chance coincidence. The higher atomic weights do not, however, approximate in any special manner to whole numbers. The smaller atomic weights $P$ may be regarded as built up of a whole number $N$ and a small fractional number $D$, so that $P = N + D$. For elements of uneven valency, $N$ is of the form $4n - 1$, and for elements of even valency of the form $4n$, where $n$ is a whole number. Exceptions to this rule are afforded by nitrogen, scandium, and beryllium. The properties of the elements are periodic functions of the values of $n$. The values of $D$ are periodic functions of the $n$ values. The twin-elements of Lorenz (Abstr., 1896, ii, 639) may be defined as elements which have the same $n$ value and whose $N$ values differ only by unity. This definition would include a number of twin-elements not given by Lorenz, as Nb – Mo, Rh – Pd, Ir – Pt, and Tl – Pb.

RICHARD LORENZ (*ibid.*, 1897, 14, 103—105), in a note on the preceding paper, calls attention to his definition of twin-elements (*loc. cit.*), and points out that this mode of classification is based on the above definition, and not on a mere approximation in the values of the atomic weights of the similar elements. H. C.

**A Graphic Representation of the Periodic System of the Elements.** By E. Loew (*Zeit. physikal. Chem.*, 1897, **23**, 1—12).—The author represents the system of elements by points upon an archimedean spiral in which $v = \phi = \sqrt{w}$, where $w$ is the atomic weight, $v$ the radius vector, and $\phi$ the polar angle. When this is done, certain allied elements fall very nearly at opposite ends of the same radius, that is, differ in position by $\pi$, for example, copper and sodium, magnesium and zinc, phosphorus, and arsenic. If the spiral be divided by a straight line through the origin, it forms segments containing groups of elements of which the corresponding members form a natural group, for example, phosphorus arsenic, antimony and bismuth. Of the last groups, the consecutive members differ very nearly by $\pi/2$ in position, and assuming this to be the true difference, the theoretical positions of the elements are obtained and found to differ but slightly from the previous values, in many cases, the differences being within the probable errors of the atomic weights. The series thus obtained represented the whole system as situated on vectors, each differing from the preceding by $\pi/16$. The vectors for elements of the same family differ by $\pi$, and those of a subsidiary allied family differ by $\pi/2$, thus lithium, potassium, rubidium, and cæsium form a family with, at $\pi/2$ intervals, sodium, copper, silver, and gold. The spiral shows certain gaps which may be filled, notably for a whole group between the chlorine and potassium groups. Helium falls in the same group as aluminium, whilst argon and fluorine are classified with the iron and platinum group. L. M. J.

**Chemical Proportions. II.** By F. Wald (*Zeit. physikal. Chem.*, 1897, **23**, 78—89.)—The author considering that his previous paper (this vol., ii, 311) has been very largely misunderstood, endeavours to give a further explanation of it, and to remove the misunderstanding. He gives an account of the axiomatic premises which underlie his paper, and emphasises the fact that he in no way endeavoured to prove the falsity of the atomic hypothesis, as he attempts to establish nothing contradictory to this hypothesis. What he does seek to show, however, is that the atomic hypothesis is not necessary to explain the laws of fixed and multiple proportions, and he states that he hopes to further show there is no necessity for its acceptance for the explanation of any of the known chemical facts. L. M. J.

**Lecture Experiment with Liquid Carbonic Anhydride.** By Carl Barus (*Amer. J. Sci.*, [iv], **32**, 1—4).—The passage of liquid carbonic anhydride through the critical temperature is best shown by using sunlight and heating the tube containing the liquid carbonic anhydride in an air bath. The projected image of the whole tube is then clear, and the demarcation between liquid and vapour is unmistakable even at a distance. Moreover, the tube acts like a cylindrical lens, a sharp, silvery focal line being obtained both for the liquid and gaseous part. The two focal lines, however, are not coincident, and hence the projecting lens must be moved backwards and forwards to obtain sharp images of the linear foci corresponding to the vapour or the liquid respectively. This displacement of the projecting lens is considerable, being from 5—6 cm. with the usual tube, and the extreme

positions of the lens remain practically unchanged with temperature, whereas it would naturally be expected that the highly compressed gas and the liquid so near the point of continuously merging into gas would show similar refracting properties; in other words, it was thought that two linear foci would be found, one corresponding with the compressed gas, and the other with the liquid, at a distance apart which would gradually vanish as the critical temperature is approached. The author believes that there is no real continuity between $CO_2$ gas and $CO_2$ liquid at the critical temperature; but there is continuity between the liquid and a gas ($C_3O_6$) which preserves the same molecule, the same molecular structure as the liquid from which it issues. Doubtless at still higher temperatures the gas with the liquid molecule will break up into the true gas with the gaseous molecule, and the fact should be indicated by the sliding lens method mentioned above.

E. C. R.

**Apparatus for Simultaneously Heating and Shaking Sealed Tubes.** By EMIL FISCHER (*Ber.*, 1897, **30**, 1485—1487).—The author describes an apparatus for keeping sealed tubes in motion whilst they are being heated. This combination of heating and shaking has been found most useful in synthetical researches in the uric acid group. The apparatus consists of a rectangular copper vessel 60 cm. long × 27 broad × 43 high, closed by a lid having two perforations, one for a thermometer, and the other for the gas-regulator. The vessel, which is three parts filled with oil or other suitable liquid, is placed on an iron stand, and heated from below. Arms are attached to the sides of the copper vessel, and on these the mechanical contrivance for the shaking rests. The arrangement is such that this part of the apparatus, together with the sealed tubes, can be removed from the vessel even during the heating. The shaking must not be too rapid, not more than 10—15 oscillations per minute. The tubes should not be more than three-quarters full, and if there is no probability of their exploding, they are simply fixed into the frame between pieces of cork by means of screws. If there is any chance of an explosion, the tubes must be carefully packed in closed iron tubes by means of cotton wool, or asbestos and the capillary point must also be protected by means of a cork.

J. J. S.

---

## Inorganic Chemistry.

**Function of Peroxides in Phenomena of Slow Oxidation.** By A. BACH (*Compt. rend.*, 1897, **124**, 951—954).—The author has made experiments with a view to ascertain whether slow oxidation is always accompanied by the formation of peroxides. The reagents used for the detection of the peroxides were titanic sulphate solution (1 gram of titanic acid dissolved in 20 c.c. of sulphuric acid and diluted to 100 c.c.), hypovanadous sulphate (1 gram of vanadic acid dissolved in 20 c.c. of hot sulphuric acid and diluted to 100 c.c.) and

the potassium dichromate, oxalic acid, and aniline method previously described (Abstr., 1895, ii, 239). It was found that peroxides are formed by the slow oxidation by air in the light or in the dark of nascent hydrogen (palladium), phosphorus, sodium, potassium, zinc, iron, lead, methylic, ethylic, and isopropylic alcohols, glycerol, formaldehyde, acetaldehyde, benzaldehyde, glucose, acetic, oxalic, and tartaric acids, ethylic ether, acetic anhydride, phenol, resorcinol, catechol, tannin, pyrogallol, dimethylaniline, diethylaniline, phenylhydrazine, formamide, acetamide, terebenthene, benzene, petroleum, quinine sulphate, morphine acetate, brucine, strychnine.

It would seem that all these compounds belonging to very varied groups are capable of forming peroxides during their slow oxidation. The oxidation involves the splitting up of the oxygen molecule $O:O$ and it may be taken that less energy is required to split it up into $\cdot O \cdot O \cdot$ than into $\cdot O \cdot$ and $\cdot O \cdot$. Consequently, in the earlier stages of the reaction, the substances combine with the grouping $\cdot O \cdot O \cdot$ and form peroxides. In some cases, tetroxides may be formed at the same time.

Peroxides may also be formed in cases of energetic oxidation. If a flame of hydrogen or carbonic oxide is directed on the surface of water, the latter afterwards gives the reactions of peroxides. In the case of carbonic oxide, percarbonic acid is produced.

When the peroxides have been formed, they help to continue and accelerate the oxidation. If air, for example, is passed through a solution of indigo mixed with terebenthene or benzaldehyde, the indigo is rapidly oxidised to isatin. Nascent hydrogen liberated from palladium produces a similar effect when oxidised by air, and in this case the indigo is completely oxidised when the quantity of active oxygen in the liquid is considerably less than that in the hydrogen peroxide that suffices to oxidise the indigo under ordinary conditions. The author considers that this result shows (1) that Hoppe-Seyler's view that the nascent hydrogen splits up the ordinary oxygen into one atom, with which it combines, and another which is set free and is capable of producing energetic oxidations, is not tenable; and (2) that the intermediate product is probably, not hydrogen peroxide, but hydrogen tetroxide.

In the blood, the readily oxidisable substances first form peroxides. and these oxidise the less readily oxidisable substances, in the same way as the peroxide formed by the terebenthene oxidises the indigo. The so-called oxidising ferments in the blood are simply readily oxidisable substances with a special aptitude for forming peroxides.

C. H. B.

**The so-called Rendering Active ("Activirung") of Oxygen and the Formation of Peroxides.** By CARL ENGLER and W. WILD (*Ber.*, 1897, 30, 1669—1681. Compare Abstr., 1896, ii, 558 and 574, and preceding abstract).—When a substance is oxidised by atmospheric oxygen in presence of a compound capable, under other circumstances, of resisting its influence, it sometimes happens that the latter is also oxidised. Attempts have been made to explain the cause of this phenomenon (*Activirung*), Schönbein regarding it as dependent on preliminary conversion of oxygen into ozone and antozone, and a similar explanation having been put forward by Brodie and by Clausius, whilst

according to the view of Hoppe-Seyler and of Baumann, nascent hydrogen appropriates one atom of the oxygen molecule, and allows the remaining one to oxidise surrounding matter. M. Traube, on the other hand, ascribes the phenomenon to the resolution of water into hydroxyl and oxygen, the latter giving rise to hydrogen peroxide (Abstr., 1893, ii, 412).

It is the authors' opinion that molecules of oxygen, and not atoms, are involved in the action, which they regard as arising from preliminary formation of the peroxides, $R_2O_2$ and $RO_2$, these compounds then acting as oxidising agents. Oxygen behaving in the above-mentioned manner is, therefore, not at first atomic, but chemically combined and easily liberated. The experiments which have led to this generalisation are described in the paper. M. O. F.

**Existence of Selenium Monoxide.** By A. W. Peirce (*Amer. J. Sci.*, 1896, [iv], 2, 163—167).—The odour of decayed cabbage which is noticed when selenium is burned in air was attributed by Berzelius to the formation of a gaseous selenium monoxide. Sacc (*Ann. Chim. Phys.*, 1847, [iii], 21, 119), was unable to obtain any evidence of the formation of selenium monoxide and referred the peculiar smell mentioned above to the formation of a small quantity of selenium hydride which would be produced when selenium is heated in the presence of moisture, and a small trace of moisture is sufficient to produce the odour.

Chabrié (*ibid.*, 1890, [vi], 20, 273) has stated that selenium, when heated at 180° in the air, undergoes an increase in weight very nearly corresponding with that required for the formation of the monoxide. The selenium which he employed was obtained from certain organic compounds by reducing the products of oxidation with sodium sulphite and hydrochloric acid. The author has heated selenium, prepared from the dioxide and dried to a constant weight at 100°, for various lengths of time at 110° to 180°, and in every experiment a loss of weight was observed. This loss is due to the volatilisation of the selenium as such. A mixture of selenium and selenium dioxide was heated in a tube at a pressure of 4 mm. at 180—200°; the contents of the tube were vaporised and maintained in that condition for 7 hours, but no gaseous products were found, and the contents of the tube possessed no odour. E. C. R.

**Atomic Weights of Nitrogen and Arsenic.** By Joseph Gillingham Hibbs (*J. Amer. Chem. Soc.*, 1896, 18, 1044—1050).—The method consists in determining the amount of metallic chloride obtained from sodium or potassium nitrate or arsenate when they are heated in a current of hydrogen chloride.

The mean of five experiments gave the atomic weight of nitrogen by the action of hydrogen chloride on potassium nitrate $N = 14{\cdot}0118 \pm 0{\cdot}000472$. With sodium nitrate, the mean of five experiments was $N = 14{\cdot}0116 \pm 0{\cdot}000741$. If these results are compared with those obtained by Penny and by Stas by treatment of potassium chloride with nitric acid, and the treatment of potassium nitrate with hydrochloric acid and also their results for the sodium salt, a close comparison can be made. Penny obtained for potassium nitrate $N = 13{\cdot}9774$, for sodium

nitrate N = 13·9906. The mean of all the author's results gives the atomic weight of nitrogen as 14·0003; when O = 16, K = 39·11, Cl = 35·45, Na = 23·05.

The determination of the atomic weight of arsenic is effected in a similar way by the action of hydrogen chloride on sodium pyroarsenate The mean of ten determinations gave As = 74·9158 ± 0·00222.

E. C. R.

**Combustion of Nitrogen.** By OTTO BLEIER (*Ber.*, 1897, 30, 1269. Compare this vol., ii, 280, and Lord Rayleigh, Trans., 1897, 181).—The nitrogen is mixed with the requisite quantity of oxygen either in an enamelled autoclave or in a thick-walled explosion pipette in which dilute alkali is placed. A considerable amount of electrolytic gas is added and then exploded, the oxides of nitrogen removed by shaking with the alkali and a further quantity of electrolytic hydrogen and oxygen added and again exploded. To remove all the nitrogen, it is necessary to repeat the operation several times. J. J. S.

**Nitrogen Chloride.** By W. HENTSCHEL (*Ber.*, 1897, 30, 1434—1437).—Nitrogen chloride dissolved in various solvents can be preserved for some time in the dark, but rapidly decomposes on exposure to a bright light. The solution in benzene is obtained by adding ammonium chloride to a 5 per cent. solution of soda which has been treated with chlorine, and agitating with benzene. About seven-eighths of the active chlorine of the aqueous solution is converted into nitrogen chloride. The solution is a clear, strongly refractive, sulphur-yellow liquid, and possesses the characteristic repulsive odour of nitrogen chloride. When exposed to sunlight, it decomposes, nitrogen being evolved and benzene hexachloride produced. The solution in carbon bisulphide yields sulphur chloride, whilst that in carbon tetrachloride simply gives nitrogen and chlorine. On the other hand, solutions in chloroform and in ether do not yield nitrogen but ammonia, ammonium chloride separating out, and hydrogen chloride and chlorine being evolved. The chloroform also yields a trace of hexachlorethane, and the ether a liquid which boils at 80—150°, contains chlorine and reduces silver chloride. A. H.

**Molecular Weight of Arsenamphide Compounds.** By EMERICH SZARVASY and CARL MESSINGER (*Ber.*, 1897, 30, 1343—1347).—Earlier vapour density determinations have shown that $2As_2O_5$ is already dissociated into $As_4O_6$ and $2O_2$ at a dull red-heat, whilst $As_4O_6$ is stable at 1560°; and that $As_2S_5$ is dissociated at about 500° into $As_2S_3$ and $S_2$, whilst $As_2S_3$ is not dissociated at 700°, but begins to be so at 1000°. It has now been found that $As_2S_2$ (normal vapour density 7·40) has a density varying from 19·16 at 450° to 6·95 at 1200°; $As_4S_3$ (normal 13·69) gives 8·20 at 792°, 6·59 at about 1000°. $As_2Se_5$ (normal 18·84) gives 9·59 at about 800°; 7·41 at about 900°; $As_2Se_2$ (normal 10·65) gives 10·54 at 900°, and 6·22 at 1050—1100°; $As_2Se$ (normal 7·92) gives numbers varying from 15·48 at 617° to 7·55 at 1159°. It will be noticed that the stability decreases in the series $As_4O_6$, $As_4S_4$, $As_4Se_2$; further, that the oxygen compounds are the most stable, the selenium ones the least so. C. F. B.

**Action of Acid Vapours on Metallic Sulphides.** By JEROME KELLEY and EDGAR FRANCIS SMITH (*J. Amer. Chem. Soc.*, 18, 1096—1098).—Arsenic trisulphide is completely volatilised in a current of hydrogen bromide; the action commences in the cold with the production of a liquid which passes out of the containing vessel on the application of a very gentle heat. Antimony trisulphide and stannic sulphide are completely volatilised in a current of hydrogen bromide or hydrogen chloride. Stannous sulphide, by the continued action of the gas in the cold, is completely converted into chloride without any volatilisation. It is, however, impossible to separate stannous and stannic sulphides by this method, as heat is necessary to drive out the stannic salt, and this causes a partial volatilisation of the stannous chloride. E. C. R.

**Arsenic Monoselenide and the Vapour Density of Selenium.** By EMERICH SZARVASY (*Ber.*, 1897, 30, 1244—1248).—The author has determined the vapour density of selenium, by V. Meyer's method, at temperatures between 774° and 1165°. At 774°, the density is 7·03, and then gradually diminishes until it becomes constant at about 900—950°, when it agrees with the formula $Se_2$ (= 5·466).

*Arsenic monoselenide*, $As_2Se$, was prepared by melting the two constituents in the requisite proportions, or with a very slight excess of arsenic, the operation being carried out in a sealed tube filled with nitrogen. The combination took place at about 600°, and the product, which consisted mainly of the monoselenide, was sublimed under pressure in an atmosphere of nitrogen. It forms black, metallic-looking crystals, giving a black streak. It is insoluble in the usual organic and inorganic solvents; concentrated hydrochloric and sulphuric acids act on it but slowly, boiling alkali hydroxides, however, decompose it in much the same manner as they do the lower sulphides of arsenic. The vapour density at 617° corresponds with the formula $As_4Se_2$, but at 1002° it corresponds with the formula $As_2Se$, and above this temperature dissociation into its elements occurs. This is the most stable of the arsenic-selenium compounds. J. J. S.

**The Amount of Carbonic Anhydride in the Atmosphere.** By W. CARLETON WILLIAMS (*Ber.*, 1897, 30, 1450—1456).—The estimations were made by a modification of Pettenkofer's method, the baryta water being filtered from the precipitated carbonate in an atmosphere free from carbonic anhydride, and the titration then effected with hydrochloric or nitric acid. Allowance was also made by means of blank experiments for the action of baryta on the glass.

The results show that the air of Sheffield (centre of the town) contains on the average 3·9 parts of carbonic anhydride in 10,000, the maximum observed in 22 estimations being 6·22 and the minimum 2·80. At a distance of 1·5 miles west of this point, the average of 142 experiments was 3·27 parts, the maximum being 5·14 and the minimum 2·16. Snow and fog clearly increase the amount present, whilst rain has no influence. Very high and very low atmospheric pressure are accompanied by an increase in the amount of carbonic anhydride, whilst the amount decreases as the temperature rises.

A. H.

**Constitution of the Metallic Carbonyls.** By ANTONIO J. FERREIRA DA SILVA (*Bull. Soc. Chim.*, 1897, [iii], **15**, 835—838).—The author discusses the results which have already been obtained by others. He is of the opinion that in the carbonyl derivatives of iron, nickel, and platinum, the carbon atoms do not form a chain, but are connected directly to the metallic atom. M. W. T.

**Influence of Pressure on the Solubility of Quartz in Water.** By GIORGIO SPEZIA (*Zeits. Kryst. Min.*, 1897, **28**, 200—201; from *Atti Accad. Sci. Torino*, 1896, **31**, 246—250. Compare Abstr., 1896, ii, 257).—Pfaff found at a temperature of 18°, and under a pressure of 290 atmospheres, one part of quartz to be dissolved in 4700 parts of water; the present author points out that, owing to experimental errors, this solubility is too high. He found that plates of quartz kept for several months in water at 27° under pressures of 1750 and 1850 atmospheres did not diminish in weight, and showed no etch figures. Pressure alone has therefore little influence on the solubility of quartz. L. J. S.

**Constitution of Metallic Alloys.** By GEORGES CHARPY (*Compt. rend.*, 1897, **124**, 957—959).—Micrographic examination shows that eutectic alloys are not definite compounds, but contain two constituents in juxtaposition in the form of extremely thin lamellæ, which are only distinguishable under high magnification. The thinness of the crystals explains the homogeneous appearance of the alloys, which often have a conchoidal fracture. It follows that eutectic alloys are analogous in constitution to the cryohydrates, and are to be regarded as mixtures of constant condensation, like mixtures of liquids which distil at a fixed temperature.

The constituent of steel, called *perlite* by Osmond, has a constitution similar to that of eutectic alloys, and this is another reason against Arnold's view that it is a definite iron carbide.

The same method of examination, however, also proves the existence of certain definite compounds. The compound $SnCu_3$ is readily recognisable in tin-copper alloys containing 5 per cent. of copper, and forms hard, white crystals, generally six-pointed stars similar to snow crystals, their proportion increasing with the percentage of copper, and ultimately constituting the whole mass when it has the exact composition $SnCu_3$. The compound $SbCu_2$ is likewise readily recognisable in copper antimony alloys. The method indicates the existence of several definite compounds that have not yet been isolated, for example, a compound of tin and antimony containing 50 per cent. of the former and isomorphous with the latter; a compound of antimony and silver containing 20 per cent. of the former and isomorphous with the latter; a compound of tin and silver containing 30 per cent. of the former and isomorphous with the latter.

In the microscopic examination of an alloy, colour, hardness, and behaviour towards various reagents are often of more value than the form of the constituents, and they often, in fact, enable a proximate analysis to be made.

There are two normal types of binary alloys. One shows crystals of a definite constituent, which may be either a single metal or a definite

compound of two, embedded in a second constituent which, as a rule, is an eutectic mixture with the structure already described. The second type contains isomorphous mixtures formed throughout its mass of a single kind of crystal, the composition and properties usually varying continuously from the exterior to the interior of each crystal. This type is somewhat common, for whilst there are a few metals that form isomorphous mixtures, there are several instances of definite compounds of two metals which are isomorphous with one of their constituents. C. H. B.

**Action of Potassium Permanganate on Cupric Bromide.** By HENRI BAUBIGNY and PAUL RIVALS (*Compt. rend.*, 1897, **124**, 954—956).—When the solution in which cupric bromide has been decomposed by potassium permanganate is evaporated to dryness and treated with water, an insoluble residue is left which, after being dried at 120—125°, contains no alkali, but cupric oxide, manganese peroxide, sulphuric anhydride, and water, in the proportions $21CuO,8MnO_2,5SO_3,18H_2O$. The sulphuric acid is wholly in combination with the copper in the form of the basic salt, $CuSO_4,3Cu(OH)_2$, whilst the remaining elements are in the proportions required to form the compound, $Cu(H_3Mn_4O_{10})_2$, corresponding with the potassium salt which is always formed when potassium permanganate oxidises carbon compounds in neutral solution. It follows that the action of the permanganate on the cupric bromide is strictly analogous to its action on carbon compounds. The complete equation is $24KBr + 8KMnO_4 + 21CuSO_4 + 18H_2O = 12Br_2 + Cu(H_3Mn_4O_{10})_2 + 5[CuSO_4,3Cu(OH)_2] + 16K_2SO_4$. The presence of an excess of cupric sulphate is necessary in order to prevent formation of the oxybromide and also to compensate for the fact that part of the copper combines with the manganese oxide. Cupric chloride is as effective from this point of view as the sulphate. An excess of permanganate is also desirable in order to ensure complete and rapid decomposition. C. H. B.

**Preparation of Aluminium Chloride.** By RICHARD ESCALES (*Ber.*, 1897, **30**, 1314—1317).—The author finds that in Stockhausen and Gattermann's method of preparing aluminium chloride, it is unnecessary to heat the aluminium throughout the reaction, since the action, when once started, is carried on by the heat arising from the combination. He therefore prepares this compound in the following way. A stream of dry hydrogen chloride is passed into a tubulated bell-jar in which a large glass dish is placed, having in the centre a glass tripod supporting a plate of asbestos, on the asbestos is placed about 20 grams of aluminium filings, the hydrogen chloride is then passed in, and the action started by pouring in a small quantity of strongly heated aluminium through the opening in the bell-jar on to the asbestos plate; the action then continues until all the aluminium has been converted into chloride. It can be collected from the sides of the jar and from the glass dish, the yield being about 70—75 per cent. J. F. T.

**Saturation of Iron by Carbon.** By HANNS VON JÜPTNER (*Chem. Centr.*, 1896, ii, 653; from *Österr. Zeit. Berg-Hütt.*, **44**, 447—449).

—Whilst the presence of manganese and chromium in iron increases its capacity of taking up carbon, on the other hand, sulphur, silicon, most metalloids, as well as phosphorus, arsenic, antimony, tin and aluminium, have an opposite effect. For pure iron, Percy gives the maximum content of iron = 4·63 per cent. corresponding with $Fe_{4\cdot4}C$. From Ledebur's data for the maximum content of carbon in iron containing various amounts of manganese and chromium, the author finds the carbon saturation power of the latter by calculation to be respectively 7·75 per cent., corresponding with $Mn_{2\cdot3}C$ and 11·6 per cent. corresponding with $Cr_2C$. These values appear to be quite independent of the iron present. The diminution in the carbon saturation power of iron caused by silicon, &c., depends probably on the substitution of the one element for the other in the ratio of their atomic weights although this power of taking up carbon is never entirely destroyed by these elements. In a carbon saturated iron containing 83·53 per cent. of iron, 5·17 manganese, 10·19 phosphorus, and 1·11 carbon, the theoretical percentage of carbon corresponding with the iron and manganese present is 4·47 per cent. Hence the presence of 10·19 per cent. of phosphorus has diminished the saturation power by 3·36 per cent., which corresponds with P : 0·85C. The author regards E. Donath's hypothesis of the presence of closed chain compounds in iron containing carbon as the best explanation, and suggests that silicon, sulphur, phosphorus, &c., may also be contained in such compounds.

E. W. W.

**Ferric Hydroxide in Precipitation.** By VERNON J. HALL (*Amer. Chem. J.*, 1897, **19**, 512—525).—The author has studied the precipitation of ferric hydroxide with reference to its effect in carrying down potassium sulphate. The results of the work show that the equation $Fe_2Cl_6 + 6KOH + 4K_2SO_4 = Fe_2(OH)_6 + 6KCl + 4K_2SO_4$, which has been suggested, does not completely represent the reaction. As was the case with aluminium, the results show the mechanical inclusion theory to be inadequate, and point towards a phenomenon of a strictly chemical nature, such as the formation of a salt of ferric hydroxide and potassium, analogous to potassium aluminate.

A. W. C.

**Tungsten Hexabromide.** By HERBERT A. SCHAFFER and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, **18**, 1098—1100).—*Tungsten hexabromide* is obtained by gently heating tungsten with bromine in an atmosphere of nitrogen. It forms bluish-black, crystalline masses, melts readily, and when carefully resublimed forms blue-black needles. It is decomposed when heated at a high temperature, fumes when brought into contact with the air, is decomposed by water with the formation of a royal-blue oxide, and dissolves in aqueous ammonia to a colourless solution.

E. C. R.

**Action of Ferric Chloride on Metallic Gold.** By PARKER C. MCILHINEY (*Amer. J. Sci.*, [iv], **2**, 293—294).—Hydrochloric acid in the presence of air is without action on metallic gold, but if a small quantity of ferric chloride is present (about $\frac{1}{50}$th of the weight of the gold) gold is dissolved. The solution is due to the action of the oxygen, which reacts with the hydrochloric acid and the gold to produce water

and gold chloride, provided that ferric chloride is present to act as a carrier of chlorine.

A mixture of hydrochloric acid and ferric chloride free from oxygen and protected from the air does not dissolve the slightest trace of gold. E. C. R.

## Mineralogical Chemistry.

**Artificial Cotunnite.** By F. STÖBER (*Zeit. Kryst. Min.*, 1897, **28**, 108—109; from *Bull. Acad. Belg.*, 1895, **30**, 345).—Very good orthorhombic crystals of cotunnite ($PbCl_2$) are deposited from a solution of lead chloride in concentrated hydrochloric acid, the crystals being grown on a glass float in the liquid. The results of detailed crystallographic and optical measurements are given. $a:b:c = 0{\cdot}5013:1:0{\cdot}8423$. Twinning on (021) is frequent. There is a fairly perfect cleavage parallel to (010). When a hot, aqueous solution of lead chloride is slowly cooled, tabular crystals are obtained, but when quickly cooled, acicular crystals result. Becquerel's "cubic" crystals of lead chloride are probably only cotunnite with the forms {100}, {010} and {001}.

L. J. S.

**Altaite from Burma.** By HENRY LOUIS (*Min. Mag.*, 1897, **11**, 215—216).—Altaite occurs in minute, crystalline grains in the gold mines at Choukpazat, Wuntho, Upper Burma, where it is associated with quartz, calcite, pyrites, mispickel and native gold. The colour is tin-white, with a somewhat yellowish tinge, and a high metallic lustre. There is a perfect cubic cleavage. The mineral appears to be brittle (altaite is usually stated to be sectile); H = 2—3. Analysis gave the results under I, and after deducting impurities, II; this agrees very closely with the formula PbTe.

| | Te. | Pb. | Fe. | Ag. | $CaCO_3$. | $SiO_2$. | Total. |
|---|---|---|---|---|---|---|---|
| I. | 34·2 | 57·4 | 0·2 | trace | 3·8 | 2·1 | 97·7 |
| II. | 37·4 | 62·6 | — | — | — | — | 100·00 |

The altaite occurs in the richer auriferous portions of the veins, and films of gold are sometimes deposited between the cleavage planes of the altaite. L. J. S.

**Nemalite from Afghánistán.** By FREDERICK R. MALLET (*Min. Mag.*, 1897, **11**, 211—214).—Specimens of nemalite from Afghánistán consist of a mass of straight, very fine, highly flexible and elastic, easily separable fibres 8 inches long, which seem clearly to have formed part of a vein in serpentine. The colour is sea-green with a silky lustre, and the fibres are inclined at an angle of about 20° to the walls of the vein. The fresh central portion gave on analysis:

| MgO. | FeO. | MnO. | CaO. | $H_2O$. | $SiO_2$. | Total. | Sp. gr. |
|---|---|---|---|---|---|---|---|
| 62·00 | 7·87 | trace | trace | 29·55 | 0·38 | 99·80 | 2·454 |

When the mineral is decomposed by hydrochloric acid, the silica is

left in a fibrous form, as is the case with chrysotile; the 0·38 per cent. of silica is therefore considered to represent 0·88 per cent. of admixed chrysotile, which may be original or secondary. The material forming the outer portions of the veins is somewhat altered, being reddish or white and opaque. It contains 0·26 per cent. of silica with some carbonic anhydride and ferric oxide, and passes into scaly hydromagnesite enclosing magnetite. L. J. S.

[Brown Spar from Goldkronach, Bavaria.] By FRIDOLIN VON SANDBERGER (*Ber. Akad. München*, 1894, **24**, 244).—In a paper (pp. 231—248) describing the ore deposits at Goldkronach near Berneck in the Fichtelgebirge, and all the minerals found there, the following analysis by Hilger is given of "brown spar" [ankerite] which is of a pale, flesh-red colour on the exterior, but is white on the cleavage surfaces. Sp. gr. 3·05.

| $FeCO_3$. | $MnCO_3$. | $CaCO_3$. | $MgCO_3$. | Total. |
|---|---|---|---|---|
| 18·470 | 3·063 | 56·066 | 21·997 | 99·596 |

L. J. S.

A Neutral "Phosphoreisensinter." By O. RAU (*Zeit. Kryst. Min.*, 1895, **24**, 613—614).—In the coal mine Königin Luise, Pachtfeld, near Zabrze, in Upper Silesia, not far from the clay slate, are cavities filled with a reddish-brown to light-yellow, glassy, transparent mineral; it is very brittle, and has a conchoidal fracture. It has no action on polarised light. Sp. gr. 2·18; H = 3—3·5. In the air, it lost 0·46 per cent. of moisture in 7 days; over sulpuric acid for 10 days, there was a loss of 12·11 per cent. At 100°, a loss of 17·69, and at 150° of 22·03 per cent. without attaining a constant weight. The mean amount of the total water was 32·01 per cent. Pieces which were clouded by the presence of numerous fractures gave slightly different amounts of water. Analyses of the transparent material are given under I and II.

| | $Fe_2O_3$. | $P_2O_5$. | $SO_3$. | $H_2O$. |
|---|---|---|---|---|
| I. | 32·05 | 20·00 | 14·38 | 33·02 |
| II. | 33·12 | 20·12 | 14·33 | 33·62 |
| III. | 0·80 | 0·00 | 10·72 | — |

Hot water extracted from the powdered mineral the amounts given under III. The formula is given as $5(Fe_2O_3,P_2O_5) + 2(Fe_2O_3,3SO_3) + 60H_2O$. This is near to diadochite, which, however, has a slight excess of iron beyond that required by the above neutral formula.

L. J. S.

Derbylite from Tripuhy, Brazil. By EUGEN HUSSAK and GEORGE T. PRIOR (*Min. Mag.*, 1897, **11**, 176—179).—The new antimonotitanate of iron (Abstr., 1895, ii, 508), which is found with lewisite in the cinnabar-bearing gravels of Tripuhy, Minas Geraes, has now been obtained in sufficient quantity for detailed determination, and it is here called derbylite.

The small orthorhombic crystals are frequently twinned on (011), giving rise to staurolite-like forms. $a:b:c = 0·96612:1:0·55025$. The mineral is pitch-black in colour, with a resinous lustre; it is trans-

lucent in very thin splinters only, and is biaxial. There is a conchoidal fracture parallel to (001). Sp. gr. 4·530; hardness about 5, but very brittle. It is insoluble in acids, but is decomposed by fusion with potassium hydrogen sulphate. The more complete of the two analyses by G. T. Prior is given below.

| $Sb_2O_5$. | $TiO_2$. | $SiO_2$. | $Al_2O_3$. | FeO. | CaO. | $Na_2O$. | $K_2O$. | Loss on ignition. | Total. |
|---|---|---|---|---|---|---|---|---|---|
| 24·19 | 34·56 | 3·50 | 3·17 | 32·10 | 0·32 | 0·76 | 0·28 | 0·50 | 99·38. |

Neglecting the silica, alumina and alkalis as due to the presence of muscovite, the formula is given as $FeO,Sb_2O_5 + 5(FeO,TiO_2)$. Details are given of the methods of analysis; the mineral was first decomposed by heating in a current of hydrogen. Lewisite and derbylite have recently been found in the cinnabar-bearing gravels enclosed in fragments of muscovite-schist. L. J. S.

**Composition of Zirkelite.** By George T. Prior (*Min. Mag.*, 1897, 11, 180—183).—The previous analysis (Abstr., 1895, ii, 508) of this new isometric mineral from Jacupiranga, Brazil, was unsatisfactory, owing to the difficulties of separation with the small amount of material then available. A new analysis on more material (0·4716 gram) gave:

| $ZrO_2$. | $TiO_2$. | $ThO_2$. | $Ce_2O_3$. | $Y_2O_3$?. | $UO_2$. | FeO. | CaO. | MgO. | Loss on ignition. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|
| 52·89 | 14·95 | 7·31 | 2·52 | 0·21 | 1·40 | 7·72 | 10·79 | 0·22 | 1·02 | 99·03. |

The formula is given as $RO,2(Zr,Ti,Th)O_2$. Sp. gr. 4·741.

The mineral was decomposed by fuming hydrofluoric acid, and the titanium estimated by Weller's colorimetric method. Full details of the methods of analysis are given. L. J. S.

**Celsian, a Barium Felspar corresponding with Anorthite.** By S. A. Hjalmar Sjögren (*Geol. Fören. i Stockholm Förh.*, 1895, 17, 578—582).—Barium felspar from Jakobsberg, Sweden, has been previously described by Igelström under the name of hyalophane, but no optical determinations were made. The mineral now described from this locality occurs in the massive state with schefferite and manganophyllite; it is clear and colourless, and shows the ordinary felspar cleavages, $c(001)$, $b(010)$, together with $m(110)$ and $M(1\bar{1}0)$ less distinct; the cleavage angle $cb$ is about $89\frac{1}{2}°$. On $c(001)$ the angle of optical extinction is 3° 10′, and on $b(010)$ 26° 45′ referred to the edge $cb$; an acute bisectrix emerges obliquely through $c$; these characters show the mineral to be anorthic. Sp. gr. 3·37; H over 6. It is easily and almost completely decomposed by hydrochloric acid. Analysis by R. Mauzelius on material dried at 110° gave:

| $SiO_2$. | $Fe_2O_3$. | $Al_2O_3$. | BaO. | CaO. | MgO. | $K_2O$. | $Na_2O$. | $H_2O$. | F. | Total less O for F. |
|---|---|---|---|---|---|---|---|---|---|---|
| 32·43 | 0·12 | 26·55 | 39·72 | 0·23 | 0·11 | 0·22 | 0·16 | 0·64 | 0·64 | 100·55. |

At 370°, 0·44 per cent. of the water is lost. This agrees closely with $BaAl_2Si_2O_8$, and it is thus an almost pure barium felspar analogous to anorthite. L. J. S.

**Phenakite from Silesia.** By Carl Hintze (*Zeit. Kryst. Min.*, 1897, 28, 174—176).—The occurrence of crystallised phenakite in

cavities of the Striegau granite is recorded. Frenzel found BeO, 45·46; $SiO_2$, 54·54 per cent., and a trace of iron. Sp. gr. 3·02.

L. J. S.

**Beryl containing Cæsium from Galicia.** By FEDERICO CHAVES Y PÉREZ DEL PULGAR and FEDERICO RELIMPIO Y ORTEGA (*Anal. Soc. Españ. Hist. Nat.*, 1895, **24**, Actas 7).—Cæsium has been detected by a microchemical reaction (with stannic chloride) in a clear crystal of light green beryl from Galicia, Spain. L. J. S.

**Gonnardite.** By ALFRED LACROIX (*Bull. soc. fran. min.*, 1896, **19**, 426—429).—The doleritic basalts near Gignat, Puy-de-Dôme, which form the plateau of Chaux-de-Bergonne, contain numerous zeolites in their cavities; one of these, which has been described as mesolite by Gonnard (*Compt. rend.*, 1871, **73**, 1147), is shown by its optical characters to be a new species, to which the name gonnardite is here given. It is white and fibrous, and forms spherical concretions about the size of a pea. The acute positive bisectrix is parallel to the length of the fibres, this character distinguishing the mineral from mesolite and thomsonite. The optic axial angle is very small and is sometimes zero; the birefringence is weaker than that of mesolite and thomsonite. The crystalline system is possibly orthorhombic. The formula, $(Ca,Na_2)_2Al_2Si_5O_{15} + 5\frac{1}{2}H_2O$ with $CaO:Na_2O = 5:3$, deduced from Pisani's old analysis, is doubtful, since, under the microscopic, the mineral is seen to be intergrown with scolecite? and sometimes with thomsonite. Gonnard has given the sp. gr. as 2·246—2·357.

L. J. S.

**Asbestos and Asbestiform Minerals.** By GEORGE P. MERRILL (*Proc. U.S. National Museum*, 1896, **18**, (1895), 281—292).—It is shown that the name asbestos, as commercially used, includes at least four distinct minerals, which only have in common a fibrous structure and more or less fire- and acid-proof properties; they are (1) tremolite or asbestos proper, (2) serpentine (amianthus), (3) anthophyllite, and (4) crocidolite. The first two of these are, as a rule, easily distinguished, but tremolite and anthophyllite are easily confused, and can only be distinguished by optical and chemical means. Of the twenty-four analyses made by the author and R. L. Packard, twelve are of anthophyllite, seven of asbestiform tremolite, and two of uralitic augite. It is considered that the fibrous structure of these minerals has been produced by a process of shearing, the original minerals being amphiboles and probably sometimes pyroxenes. L. J. S.

**Mica from Co. Dublin.** By J. P. O'REILLY (*Min. Mag.*, 1897, **11**, 199—210).—The white mica of the Three Rock Mountain, Co. Dublin, often encloses, zonally arranged, black and brown specks which sometimes show hexagonal outlines, and may possibly be melaconite. The microscopic characters of blue and green spots are also described in detail. After the separation of the black particles, the white mica gave analysis I by Miss M. W. Robertson: at 100°, there is a loss of 0·2506, and between 100—240° of 0·1058 per cent. Hydrochloric acid dissolves out the colouring matter from the black particles, leaving a residue of white mica, the soluble portion consisting of 9·78—22·5

$Cu_2O$, and 25·35—45·14 $Fe_2O_3$ per cent. In a note by W. N. Hartley it is stated that there were no black specks, but only bright red spangles, in the material analysed, and that the copper was shown to be present as cuprous and not as cupric oxide.

| | $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MnO. | $Cu_2O$. | CaO. | MgO. |
|---|---|---|---|---|---|---|---|---|
| I. | 39·414 | 33·738 | 1·418 | — | 1·244 | 3·654 | 0·955 | 1·344 |
| II. | 42·99 | 34·44 | — | 2·69 | 0·06 | 0·10 | 0·54 | 0·77 |

| | $K_2O$. | $Na_2O$. | $Li_2O$. | F. | Loss on ignition. | Total. |
|---|---|---|---|---|---|---|
| I. | 9·430 | 2·675 | 0·642 | trace | 4·710 | 99·224 |
| II. | 13·29 | trace | — | — | 5·05 | 99·91 |

Analysis by C. Darling of a mica containing copper from Glencullen, Co. Wicklow, is given under II. L. J. S.

[Forsterite, Hornblende, Nontronite, Batavite, and Garnet from Bavaria.] By Ernst Weinschenk (*Zeit. Kryst. Min.*, 1897, **28**, 135—164).—Various minerals which occur in connection with the graphite deposits in the gneiss to the north of Passau are described; analyses are given of the following. Blue quartz occurs, with other minerals, embedded in the graphite itself; when treated with hydrofluoric acid, there was a residue of 0·056 per cent. which contained iron and manganese. In the associated metamorphic limestone are, amongst other minerals, colourless forsterite (anal. I) and crystals of hornblende ("pargasite," anal. II); in I is included a residue of 1·92 per cent. which was unattacked by hydrochloric acid. Nontronite occurs in the syenites as a decomposition product and as pseudomorphs after hornblende; after deducting hornblende, its composition is given under III, from which the formula is deduced as $H_4Fe_2Si_2O_9$. Owing to the hygroscopic nature of the material, the water given off at 110° varies from 5·00 to 10·62 per cent.; the remainder of the water, which is that shown in the analysis, is given off on ignition. The optical characters agree with monoclinic symmetry. *Batavite* is the name given to a white, scaly decomposition product which occurs with the nontronite and with kaolin. It closely resembles nacrite (kaolin) in appearance, but differs from it in giving a bulky precipitate of magnesia when decomposed by a solution of caustic soda. The mean of two analyses on material dried at 110° is given under IV, from this the formula is given as $2[Al(OH)_2]4(MgOH)Si_4O_{13}$. It appears to be somewhat related to the micas, and under the microscope sometimes shows hexagonal outlines.

| | $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MnO. | CaO. | MgO. | $Na_2O$. | $H_2O$. | Total. | Sp. gr. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| I. | 43·37 | — | — | 4·17 | 1·41 | 0·00 | 48·40 | — | — | 99·27 | 3·242 |
| II. | 46·38 | 15·33 | 0·00 | 1·51 | — | 13·14 | 20·24 | 1·78 | 1·21 | 99·59 | 3·048 |
| III. | 38·97 | 1·26 | 48·34 | — | — | — | — | — | 11·43 | 100·00 | — |
| IV. | 42·33 | 16·35 | — | — | — | — | 28·17 | — | 13·19 | 100·04 | 2·183 |
| V. | 48·58 | 17·52 | 4·74 | 0·00 | trace | 11·21 | 13·24 | — | 5·00 | 100·29 | 3·052 |
| VI. | 36·88 | 19·58 | 2·14 | 13·48 | 27·14 | 1·71 | — | — | — | 100·93 | — |
| VII. | 38·77 | 19·32 | 36·67 | | trace | 4·17 | — | — | — | 98·93 | — |

A mineral from Bodenmais, which has been called anthrophyllite, is shown to be common hornblende (anal. V) with the formula $3R''_4Si_4O_{12} + 2R''_4R'''_4Si_2O_{12}$. Spessartite, which occurs as isotropic crystals in pegmatite near Aschaffenburg (compare Abstr., 1896, ii,

310, 312), gave analysis VI, by E. Schröder. Almandine from granite near Aschaffenburg gave VII, by O. Wehr. L. J. S.

**Tourmaline from Caprera, Sardinia.** By Domenico Lovisato (*Zeit. Kryst. Min.*, 1897, **28**, 183; from *Atti R. Accad. Lincei*, Rend. 1895, [v], 4, (1), 84—87).—Tourmaline, which has previously been known from only one locality in Sardinia, has been found by the author at several places in the orbicular granite and in the adjacent schists and gneisses. On the island of Caprera, it occurs as black crystals of sp. gr. 2·95—3·05; analysis by M. Fasolo, on material containing some quartz, gave

| $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | $Mn_2O_3$. | MgO. | CaO. | $Na_2O$. | $B_2O_3$. | F. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|
| 40·09 | 36·41 | 8·16 | 1·56 | 0·79 | 2·40 | 0·28 | 1·25 | 7·14 | 1·93 | 100·01 |

At a dull red heat there is a loss of 2·15 per cent. Potassium was detected spectroscopically. L. J. S.

**[Hedenbergite and Epidote] from Sardinia.** By Domenico Lovisato (*Zeit. Kryst. Min.*, 1897, **28**, 184—185; from *Atti R. Accad. Lincei*, Rend. 1895, [v], 4, (1), 111—116).—In the schists of Su Porru, between Fonni and Cereboi, is a mineral having the appearance of epidote but which is shown by the analysis (I) of Fasolo to be hedenbergite with the formula $2MnO,3FeO,5CaO,10SiO_2$. Before the blowpipe it fuses to a black, magnetic mass. It is decomposed by warm hydrochloric acid, giving a yellow solution, gelatinous silica, and an insoluble residue.

In the same rock are greenish-yellow, translucent needles, which are shown by Fasolo's analysis (II) to have the formula

$$MnO,8CaO,Fe_2O_3,6Al_2O_3,16SiO_2,$$

and so to be epidote poor in iron. In the older trachyte are spheroids which in the interior consist of green, translucent epidote; analysis by Frasolo gave the results under III; the loss of 2·83 per cent. takes place between 210° and red heat.

| | $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MnO. | CaO. | MgO. | $Na_2O$. | $TiO_2$. | $H_2O$. | Total. | Sp. gr. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I. | 48·48 | — | — | 17·46 | 10·92 | 22·62 | 0·32 | — | — | 0·32 | 100·12 | 3·446 |
| II. | 41·97 | 28·60 | 5·48 | — | 3·10 | 19·55 | trace | — | — | 0·71 | 99·41 | 3·126 |
| III. | 42·25 | 20·35 | 11·87 | 0·31 | — | 18·65 | 2·13 | 1·47 | 0·02 | 2·83 | 99·88 | 3·04–3·16 |

Epidote is found in all the crystalline rocks of Sardinia.

L. J. S.

**Simple Massive Minerals.** By John W. Judd (*Min. Mag.*, 1895, **11**, 56—63).—Several simple crystalline rocks, each composed essentially of a single mineral, are described; these include a purple corundum rock from Pipra in South Rewah, India, and a grey corundum rock from the Mysore State; a fibrolite rock and a tourmaline rock from India; a green garnet rock and a picotite rock, which occur as dykes in the serpentine at Bingera, New South Wales. The black tourmaline or schorl rock is dull and fibrous and in part velvety, and under the microscope is seen to consist of small, acicular crystals of tourmaline. An analysis gave:

| $SiO_2$. | $Al_2O_3$. | FeO. | CaO. | MgO. | $Na_2O$. | $Li_2O$. | $H_2O$. | $B_2O_3$. | Total. |
|---|---|---|---|---|---|---|---|---|---|
| 35·94 | 31·22 | 9·23 | 1·66 | 5·53 | 3·96 | trace | 3·55 | 9·08 | 100·17 |

Fluorine, phosphoric acid, manganese, potassium and titanium are absent. Sp. gr. 3·02—3·11. L. J. S.

**Andradite from Ontario.** By BERNARD J. HARRINGTON (*Canadian Record Sci.*, 1896, **6**, 479—481).—The magnetite of the "Paxton Iron Mine," Lutterworth township, Ontario, is associated with garnet, pyroxene, hornblende, &c. The garnet is black, and is mostly massive, but also in crystals. Sp. gr. 3·813. Analysis gave:

| $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MnO. | CaO. | MgO. | Loss on ignition. | Total. |
|---|---|---|---|---|---|---|---|---|
| 35·68 | 5·88 | 23·70 | 3·65 | 0·81 | 29·64 | 0·35 | 0·28 | 99·99 |

This reduces to the garnet formula. Titanium is absent. L. J. S.

**Synthesis of Iron Silicates.** By FEDERICO CHAVES Y PÉREZ DEL PULGAR (*Anal. Soc. Españ. Hist. Nat.*, 1896, **24**, Actas 157—158).—The following experiment was made in connection with the study of glauconite. A syrupy solution of sodium silicate and small fragments of ferrous sulphate were kept in an open vessel for 20 months, water being added as evaporation took place. Besides sodium sulphate, white grains and a greenish-grey, crystalline powder were formed; these were insoluble in water, but decomposed by nitric acid with separation of pulverulent silica, the solution containing iron, sodium, and potassium (the potassium was introduced as an impurity in the sodium silicate). L. J. S.

**Analysis of a Barytes Rock.** By FEDERICO CHAVES Y PÉREZ DEL PULGAR (*Anal. Soc. Españ. Hist. Nat.*, 1895, **23**, Actas 260—261).—A grey, compact, granular barytes rock from Peñaflor, Seville, described by Calderón (*Anal. Soc. Españ. Hist. Nat.*, 1894, **23**, 20) gave on analysis:

| $BaSO_4$. | $Fe_2O_3$. | $H_2O$ (at 170°). | $SiO_2$, Ca, Alkalis. | Al, Mn, Co. |
|---|---|---|---|---|
| 80·6505 | 16·7752 | 0·0320 | not estimated. | traces. |

Sp. gr. 4·02. Thin sections under the microscope show plates of barytes, with magnetite, and as accessories, calcite, leucoxene, garnet, chlorite and felspar. L. J. S.

**Gypsum Rocks from Kansas.** By EDGAR H. S. BAILEY and W. M. WHITTEN (*Kansas Univ. Quart.*, 1897, **6**, A, 29—34).—Seven analyses are given of average commercial samples of gypsum rock and "dirt," which are quarried and mined in Kansas for the manufacture of cement. Besides calcium sulphate and water, the rock contains only small quantities of silica, iron oxide, alumina, magnesia, and carbonic anhydride. The "dirt," which is a light brown, soft, disintegrated material, is less pure. L. J. S.

**Clay.** By JEFFERSON MIDDLETON (17*th Ann. Rept. U.S. Geol. Survey* (for 1895—6), 1896, Part III., 816—880).—In this report on "the statistics of the clay-working industries of the United States," several analyses of clay, commercial felspar, &c., are given. L. J. S.

**Permian and Triassic Rocks from near Liverpool.** By PHILIP HOLLAND and EDMUND DICKSON (*Proc. Liverpool Geol. Soc.*, 1896, **7**, 443—452).—Analyses are given of marls and sandstones of Permian and Triassic age from the neighbourhood of Liverpool; they were made

with the object of ascertaining the source of the rocks, and of determining the nature and amount of the cementing material. The fine material between the grains of the sandstones was separated and shown to consist mainly of small splinters of quartz, with some mica and felspar, but very little clay and no carbonates; traces of barium sulphate were sometimes present. L. J. S.

**Meteoric Iron from Forsyth Co., Georgia.** By EMIL W. COHEN (*Sitz.-Ber. Akad. Berlin*, 1897, 386—396. Compare Abstr., 1896, ii, 375).—This iron is remarkable, since it shows in the same mass two distinct structures; these are sharply separated from each other, but have intricate boundaries. One portion has a granular structure, and the grains, which are all $\frac{1}{4}$—$\frac{1}{2}$ mm. diam., themselves consist of grams 0·02—0·03 mm. diam., some of which are more readily etched than others; the other portion of the iron appears to be almost compact, and consists of grains 0·02 mm. across. The granular variety is easily etched by dilute acid, whilst the compact variety is only slowly attacked even by strong acids. Accessory constituents are comparatively rare, and are mostly confined to the compact portion; troilite is the most frequent, but graphite, schreibersite, and small, spindle-shaped bodies are also present. The iron, especially the granular variety, rusts very quickly, this being due to the presence of lawrencite, which oozes out on the surface in greenish drops and is then oxidised to ferric chloride and oxychloride. From the rust, 3·55 per cent. of chlorine was extracted by water, and 4·99 per cent. by sulphuric acid. Analyses were made by O. Sjöström of the granular (anal. I) and compact (II) varieties, taken from widely separated portions of the mass, and free from visible accessories and rust.

| | Fe. | Ni. | Co. | Cu. | C. | S. | P. | Cl. | Total. |
|---|---|---|---|---|---|---|---|---|---|
| I. | 94·18 | 5·56 | 0·60 | 0·02 | 0·04 | 0·05 | 0·19 | 0·17 | 100·81 |
| II. | 94·03 | 5·55 | 0·53 | not est. | 0·02 | 0·03 | 0·23 | trace. | 100·41 |

The granular portion was tested for manganese and chromium, but with negative results. The corresponding mineralogical composition is:

| | Nickel-iron (Kamacite). | Schreibersite ($Fe_2NiP$). | Troilite (FeS). | Lawrencite ($FeCl_2$). | Sp. gr. |
|---|---|---|---|---|---|
| I. (Granular). | 98·33 | 1·23 | 0·14 | 0·30 | 7·3357 |
| II. (Compact). | 98·42 | 1·49 | 0·08 | 0·01 | 7·4954 |

As the composition of the two varieties is essentially the same, the differences in sp. gr. and the action of acids can only be due to differences of structure. The low sp. gr. is due to the porosity of the iron, which is also indicated by the presence of enclosed gases.

Like the Locust Grove iron (this vol., ii, 272), this iron belongs to the rare group of meteorites called "ataxite" by the author. Accessories are small in amount, and apparently do not include cohenite, chromite and daubréelite. The differences in structure must be due to the rate of cooling, and the fragment found is probably only a portion of a mass originally larger. L. J. S.

**The Bendegó Meteorite.** By ORVILLE A. DERBY (*Archivos Museu Nacional, Rio de Janeiro*, 1896, 9, 87—184).—This iron, found in

1784, weighs 5360 kilos., and has the extreme dimensions 2·2 × 1·45 × 0·58 metres; it is now in the Rio de Janeiro Museum. Detailed accounts are given of the history and external form. Some planes of easy fracture, which mark the junctions of different crystalline individuals of the iron, are called "Wollaston planes." With the exception of troilite-nodules and patches of cohenite, the iron consists essentially of kamacite, there being very little tænite (about 0·1 per cent.) and probably no plessite, so that the Widmanstätten figures do not stand out in relief on the etched surface, but are visible as an oriented sheen. On the etched surfaces of the kamacite individuals are the so-called file markings, together with systems of fine raised lines, called "Bendegó lines," which are apparently due to lamellar twinning (parallel to the faces of the hexakisoctahedron {421}) as are the Neumann lines of hexahedral irons. Analysis of the bulk of the iron, which represents almost pure kamacite, gave I (by Dafert), and a partial analysis by G. Florence is given under II; this agrees with the usual formula, $Fe_{14}Ni$, for kamacite. The troilite gave the results under III (also a trace of silica); the residue probably consists of daubréelite and schreibersite. Cohenite is abundant, and is seen on the cut surface as embroidery-like patches; measurements by E. Hussak of the imperfect crystals show them to be isometric: sp. gr. 6·1805; analysis IV, by Dafert, after deducting 5·72 per cent. of schreibersite. The schreibersite and rhabdite gave analysis V (also a trace of tin); measurements are given of the tetragonal rhabdite needles. Analyses were made of another phosphide of iron and nickel of uncertain nature, which remains as a black powder when the iron is dissolved in dilute acid. Some chromite, rich in crystal faces, hypersthene and "magnetic globules" are also present. Carbon was shown to be absent in the gas evolved when the iron is dissolved in dilute acid.

| | Fe. | Ni. | Co. | Cu. | P. | C. | S. | Insol. | Total. |
|---|---|---|---|---|---|---|---|---|---|
| I. | 93·06 | 6·83 | | — | trace | — | — | 0·33 | 100·22 |
| II. | — | 6·36 | 0·79 | 0·0045 | — | — | — | — | — |
| III. | 62·51 | trace | trace | — | — | — | 33·24 | 5·26 | 101·01 |
| IV. | 90·16 | 3·62 | | — | trace | 6·39 | — | — | 100·17 |
| V. | 52·42 | 33·51 | | 0·25 | 15·09 | — | — | — | 101·27 |

L. J. S.

[Hungarian Ores, Waters, &c.] By ALEXANDER VON KALECSINSZKY (*Jahresber. k. ung. geol. Anstalt*, 1894 (for 1892), 197—201; 1895 (for 1893), 170—176).—In these annual reports of the work done in the chemical laboratory of the Hungarian Geological Institute, analyses of rocks, ores, waters, coals, &c., are given. L. J. S.

Argentine Waters. By JUAN J. J. KYLE (*Anal. Soc. Cient. Argentina*, 1897, **43**, 19—25, 111—121, 161—171, 280—285).—The results of numerous analyses of waters from rivers, streams, surface and artesian wells in Argentina are given. L. J. S.

## Physiological Chemistry.

**The Relation of the Respiratory Exchanges to Temperature in Cold-blooded Animals.** By HORACE MIDDLETON VERNON (*J. Physiol.*, 1897, 21, 443—496).—In cold-blooded animals, the carbonic anhydride discharge does not vary directly with rise and fall of temperature. There are ranges in which metabolism remains nearly constant; this range is most marked in newts and earthworms, and comprises from 10° to 22·5° on warming, and a rather shorter range on cooling, the animals. The same is true for either a somewhat shorter or a somewhat different range in toads, blindworms, axolotls, and frogs. In *Rana temporaria*, the range is much shorter, 12·5° to 17·5°. In snails, the discharge increases from 2° to 20°, and then remains constant up to 30°. In the cockroach, the metabolism increases uniformly with the temperature.

In frogs, this was found to be due to a nervous mechanism in the bulb, since division of the brain above, and of the cord below the bulb, respectively do not and do abolish the range of constancy. Curare, however, unless given in excessive doses, does not abolish it. Morphine has but little action; strychnine causes a rapid increase of carbonic anhydride discharge on warming from 2° to 10°, but from this point up to 30° it remains constant. Veratrine causes the discharge to be constant up to 22°, beyond which point it increases much more rapidly than in normal frogs. Taking the average carbonic anhydride discharge of normal frogs from 2° to 30° as 1, that of the cockroach is 3·03, of the newt 1·6, of the toad 1·32, axolotl 1·14, snail 0·88, *Rana esculenta* 0·74, blindworm 0·52, earthworm 0·45, frogs with the cord divided just below the bulb 0·5 to 0·65, curarised frogs 0·43 to 0·58, according to the dose, strychnised frogs 2·56, and veratrinised frogs 1·22.

The mean respiratory quotient for both normal and curarised frogs is 0·85, frogs with the bulb divided at either its upper or lower border 0·94, strychnised frogs 1·22. The other animals examined had quotients varying from the maximal value of 0·9 for the earthworm to one of 0·72 for the blindworm. W. D. H.

**Increased Absorption of Oxygen by the Blood, and the Therapeutic Use of Oxygen.** By GEORG KASSNER (*Chem. Centr.*, 1896, ii, 307; from *Apoth. Zeitung*, 11, 404—405).—The use of oxygen rather than compressed air is recommended in disease, as arguing principally from the high percentage of oxygen in the swimming-bladder of fishes, the blood appears to have the power of taking up more oxygen than nitrogen by absorption, and to take up more oxygen than is necessary for the life of the organism, such surplus being available on emergencies. W. D. H.

**Osmotic Pressure as the Cause of Exchanges between Red Blood-corpuscles and Salt Solutions.** By HANS KOEPPE (*Pflüger's Archiv*, 1897, 67, 189—206).—The behaviour of red blood-corpuscles

in solutions of urea, ammonium carbonate, ammonium chloride, and other salts is in accord with the hypothesis that osmotic pressure comes into play between blood-corpuscles and blood-plasma, and that the osmotic pressure gives the measure of the volume of the blood discs. Small exceptions to this rule, noted when solutions of chloride and carbonate of sodium or potassium are employed, are explicable on the "theory of solutions" of van't Hoff and the "theory of electrical dissociation" of Arrhenius. W. D. H.

**Physiological Action of certain Ethereal Salts.** By G. VOGEL (*Pflüger's Archiv*, 1897, **67**, 141—162).—The following substances were injected intravenously in rabbits: ethylic formate, ethylic acetate, isobutylic acetate, amylic acetate, ethylic propionate, ethylic butyrate, isobutylic butyrate, ethylic valerate, amylic valerate, ethylic œnanthate, ethylic sebacate. In small quantities, they quickly cause an energetic increase of the respiratory activity. In large doses, they paralyse the nerve centres without preceding convulsions.

W. D. H.

**Influence of β-Tetrahydronaphthylamine on the Body Temperature.** By JOHN FAWCETT and W. HALE WHITE (*J. Physiol.*, 1897, **21**, 435—442).—Stern (*Virchow's Archiv*, 1889, **115**, 14) called attention to the fact that this drug causes a rise of temperature in rabbits. This is confirmed in the present research; 3 or 4 c.c. of a 3 per cent. solution injected under the skin causes pyrexia, a rise of from 2 to 5°, occurring within two or three hours. There is, simultaneously, increase in the rapidity of the heart and respiration. In animals poisoned by curare, or kept alive by artificial respiration after division of the spinal cord high up, this does not occur. Curare, and the operation, and even artificial respiration when the animal is etherised and tied down, produce a fall in temperature. The way in which the drug produces fever is therefore uncertain. It is, however, not due to increased muscular activity. W. D. H.

**Changes which some Acids of the Oxalic Series undergo in the Organism.** By PIO MARFORI (*Chem. Centr.*, 1896, ii, 106; from *Ann. Chim. Farm.*, **23**, 193—203).—Malonic acid, given either as such or as the sodium salt, passes only in small quantities into the urine; it leads to an increase of the urinary carbonates. Barbituric acid also arises from it, as oxaluric does from oxalic acid. Succinic acid does not pass into the urine. Glutaric acid passes only in small quantities into the urine; the greatest part is oxidised, and lessens the urinary acidity. No increase of volatile fatty acids was observed as the result of administering these dibasic acids. W. D. H.

**Occurrence of Hydrogen Sulphide and Indole in the Human Stomach.** By HERMANN STRAUSS (*Chem. Centr.*, 1896, ii, 109; from *Berl. klin. Woch.*, **33**, 385—389).—Certain cases of disordered digestion resulting from obstruction are described in which colonies of bacteria (of the *Bacterium coli* group) obtained from the stomach, produced indole and hydrogen sulphide. This can be produced in a peptone solution with or without the presence of sugar.

In other cases, hydrogen sulphide was absent, and the smell

produced was like that of putrid cheese. A back-flow of pancreatic juice into the stomach was suspected in some cases. W. D. H.

**Action of Suprarenal Extracts.** By SWALE VINCENT (*Proc. physiol. Soc.*, 1897, 25—26).—Large doses of extracts of the suprarenals of mammals, injected subcutaneously, cause death; the most marked symptom is muscular paralysis, of central origin. Blood in the urine, and from the nose, occasionally convulsions, and fall of temperature, were also observed. Glycerol extracts cause local ulceration. Extracts of the cortex of the gland, or of the liver, spleen, and kidney are inactive. After a sub-fatal dose, a partial immunity is set up.

W. D. H.

**Effect of Work on the Quality and Composition of Cows' Milk.** By P. DORNIC (*Bied. Centr.*, 1896, 26, 197—198; from *Milchzeit*, 1896, 331, and *L'ind. Latière*, 12 April, 1896).—Experiments lasting two weeks were made with two cows, which were used for ploughing for the first week, and rested the second week. During the period of work, the cows received, besides the usual food, 1 kilo. of rye per head per day. The effect of work on the composition of the milk was only slight. The dry matter and acid increased a little, whilst the yield of milk diminished slightly. The milk produced during the period of work frequently curdled at 45°, whilst that obtained during the period of rest curdled at 70—75°. N. H. J. M.

**The Reason why Milk Coagulates when Heated.** By BRUNO BARDACH (*Monatsh.*, 1897, 18, 199—216).—About 12 hours' heating at 100° is necessary to coagulate quite fresh milk; at 150°, 3 minutes suffice. Most of the experiments were carried out at 130°, at which temperature 1 hour's heating is necessary. It was found that but the merest traces of volatile (formic) acid are formed; further, that the total acid formed is insufficient to coagulate the milk at the ordinary temperature. When a 5 per cent. solution of lactose is heated for 1 hour at 130°, no acid is formed; if 0·5 per cent. of sodium hydrogen phosphate is added in addition, then the reaction is found to have changed from alkaline to acid. A 4—8 per cent. solution of casein in water containing 0·4—0·8 per cent. of sodium hydrogen phosphate is unchanged when it is heated for a short time with the lactose solution that has been heated for an hour already; if the casein solution has also been heated for an hour previously, then coagulation at once takes place when the two solutions are heated together, and if a freshly made solution containing casein, lactose, and sodium hydrogen phosphate is heated for an hour, coagulation takes place. The coagulation that milk undergoes when heated is thus a complex process; coagulation is brought about by the action, at the high temperature, of the small quantities of acid formed from the lactose, but these are powerless to coagulate the original, unchanged casein, and it is only after the casein itself has also been changed by the heating that it becomes coagulated. C. F. B.

**The Proteids of Cows' Milk.** By KARL STORCH (*Monatsh.*, 1897, 18, 244—281).—If cows' milk is freed from fat by skimming after it has remained for 24 hours, or after it has been centrifugalised,

and is then mixed with three times its volume of a saturated solution of sodium sulphate and a few drops of egg-albumin, and heated to 100°, coagulation takes place. When the filtrate from the coagulum is carefully neutralised with a saturated solution of sodium sulphate to which a very little acetic acid has been added, and is then stirred with excess of solid sodium sulphate, a substance, *a*, is salted out; in the filtrate from this, another substance, *b*, can be precipitated by the addition of strong acetic acid; if this is filtered off, the filtrate is now found to be free from proteids. If the milk, without previous coagulation, is at once saturated with solid sodium sulphate, *a* separates as before, and in the filtrate from it, acetic acid precipitates *b*, but the filtrate from this is now found to contain a proteid, which must be the lactalbumin of other authors (mixed, perhaps, with lactoglobulin, assuming that such a substance can really be obtained from milk). It is thus evident that, in the first method, the lactalbumin (and lactoglobulin) is removed by the preliminary coagulation. Both *a* and *b* contain phosphoric acid. *a* contains calcium, and is soluble in water; it is precipitated from the aqueous solution by the addition of acetic acid, but it is then free from calcium, and is insoluble in water, although soluble in very dilute solutions of alkalis; it has the character of a caseinogen, and is coagulated when it is warmed with rennet extract. *b* contains no calcium, and is insoluble in water, but soluble in very dilute alkalis; it is not appreciably coagulated by rennet.

As regards the power of salting out possessed by sodium sulphate, no precipitate can be obtained at the ordinary temperature when, not the solid salt, but a concentrated solution of it is used, no matter how much is added; at 50°, 19 volumes of the solution to 1 of the milk suffice to produce a precipitate; at 100°, 1 volume suffices. Magnesium sulphate may also be used for salting out; of a saturated solution of this salt, $\cdot 1\frac{1}{2}$, $\frac{2}{3}$, and $\frac{1}{8}$ volumes suffice to produce a precipitate respectively at the ordinary temperature, 50°, and 100°. Sodium chloride may also be used; the numbers in this case are 8 and 2 volumes respectively at 50° and 100°; at the ordinary temperature, no precipitate can be produced by use of a saturated solution. When, however, magnesium sulphate or sodium chloride is used in the same way as sodium sulphate, *a* is found to be precipitated in the preliminary coagulation with egg-albumin, but the lactalbumin (and lactoglobulin) is not so precipitated, but remains in the filtrate from *b*. If, on the other hand, the preliminary coagulation is carried out with sodium sulphate and egg-albumin as at first, *a* can then be salted out from the filtrate with either magnesium sulphate or sodium chloride, and, in the filtrate from it, *b* can be separated as usual. In all cases the weight of *a* obtained is 0·47—0·56 gram from 20 c.c. of milk; of *b*, 0·05—0·08 gram.

After preliminary coagulation with sodium sulphate and egg-albumin, acetic acid produces a precipitate equal in weight to *a* and *b* together, and the filtrate contains no proteids. But a large quantity of acetic acid is necessary for this; otherwise the precipitation is only partial, and from the filtrate *a* and *b* can be obtained by successive treatment with sodium sulphate and acetic acid. The presumption is,

then, that the substance precipitated by acetic acid from the original milk is the true caseinogen, and that it is decomposed by metallic salts into the substances *a* and *b*. These two substances can be salted out together by saturating the milk with two of the salts at the same time; or one can be salted out with one salt, and, in the filtrate from it, the other can be salted out with another salt. C. F. B.

**Action of Oxalic Acid and its Derivatives on the Kidneys.** By WILHELM EBSTEIN and ARTHUR NICOLAIER (*Virchow's Archiv*, 1897, **148**, 366—388).—The investigation was undertaken with a view to the artificial production of urinary calculi. This was not accomplished, and the present communication relates to the action of oxalic acid and certain of its derivatives on the kidneys when administered in a succession of small doses to dogs and rabbits. Oxalic acid was found to cause the appearance of a deposit of calcium oxalate in the urinary tubules; these deposits are frequently visible to the naked eye. Oxamic acid is eliminated as a calcium salt in the urine. A similar result followed the administration of ammonium oxamate and oxamaethane; the kidneys were usually healthy. The administration of oxamide did not lead to the deposition of concretions; in many cases, the kidneys, however, were of the granular contracted kind. W. D. H.

**The Work of Digestion and the Excretion of Nitrogen in the Urine.** By N. V. RIAZANTSEFF (*Chem. Centr.*, 1896, ii, 746; from *Arch. des Sci. biol. St. Petersburg*, **4**, 393—414).—The increase in the urinary nitrogen which immediately follows a meal is believed to be due to the increased work of digestion. Foods which produce an increased activity of the secreting glands act in this way more efficaciously than those which produce less activity, but even acidified water (introduced, in a dog, into the stomach by a fistula) causes the glands to secrete, and this is followed by a rise in the nitrogen excreted in the urine. W. D. H.

**Acetonuria.** By FELIX HIRSCHFELD (*Chem. Centr.*, 1896, ii, 394—395; from *Centr. klin. med.*, **17**, 617—620).—In healthy persons, a diet of proteid and fat leads to an increase of acetone in the urine. The addition of carbohydrate to the diet causes this to disappear. This is explained by its "sparing" action on proteid metabolism. The same holds in the acetonuria of disease, and explains the occurrence of acetone in diabetics, in whom carbohydrate metabolism is upset.

W. D. H.

**Poisonous Action of Sulphurous Acid and its Salts, and the Admissibility of their Use in Foods.** By HEINRICH KIONKA (*Chem. Centr.*, 1896, ii, 902; from *Zeit. Hyg.*, **22**, 351—397).—The "meat preserve crystals" prepared by Heyden and Co. contain 7·5 per cent. of sulphurous acid. This led to an investigation of this gas and its compounds as a poison. Contained in the inspired air, quite small quantities prove fatal. Small doses (0·02 to 0·04 gram) of sodium sulphite injected into frogs paralyse the heart, the central, and to some extent the peripheral nervous system. Dogs fed on the salt, or on food preserved by its use, suffer from injuries to various organs, especially

the lungs and kidneys; there is local irritation of the stomach, and a fall of blood pressure, and hæmorrhages tend to occur. The use of the salt as a preservative is most reprehensible. W. D. H.

---

## Chemistry of Vegetable Physiology and Agriculture.

---

**Fermentability of Galactose.** By A. BAU (*Bied. Centr.*, 1896, **26**, 213—214; from *Zeit. Spiritus Ind.*, 1896, Nos. 38 and 39).—*d*-Galactose is not fermentable by *Saccharomyces productivus*, *S. membranæfaciens*, *S. apiculatus*, and *Schizosaccharomyces Pombe*. Under suitable conditions, it is completely fermented by *Saccharomyces cerevisiæ*, by *S. Logos*, *S. Pastorianus I*, *II*, and *III*, *S. ellipsoideus I* and *II*, *S. Marxianus*, lactose yeast, and also, but only slowly, by *Monila candida*. *d*-Galactose ferments with greater difficulty than *d*-glucose.

N. H. J. M.

**Effect of Temperature on the Production of Free Oxalic Acid in Cultivations of Aspergillus niger (van Thiegh).** By CARL WEHMER (*Bied. Centr.*, 1896, **26**, 191—192; from *Ber. deut. bot. Ges.*, 1896, 163).—*Aspergillus niger*, on peptone solution, produces free oxalic acid abundantly in presence of potassium, sodium, calcium, and ammonium nitrates, and ammonium phosphate, but not in presence of ammonium sulphate and chloride.

With ammonium nitrate, the amount of oxalic acid increases at 15—20°, and is gradually destroyed by the fungus. At 33—35°, free cxalic acid is no longer formed, but oxalates are sometimes found in small quantities. When calcium carbonate is added, calcium oxalate is produced in considerable amount, but under these conditions the fungus does not thrive.

When the fungus is cultivated on ammonium tartrate, the production of spores ceases at 33—35°. Oxalic acid could not be detected, and the liquid showed an alkaline reaction, the tartrate being converted into carbonate. In sugar solutions, free acid is formed in abundance at 8—10°, but is destroyed at a higher temperature (15°).

The change in amount of acid observed in *Crassulaceæ* during night and day is probably due to the change of temperature, the acid accumulating in the night and being destroyed in the daytime.

N. H. J. M.

**Latent Vitality of Seeds.** By J. GIGLIOLI (*Ann. Agron.*, 1897, **23**, 190—191; from *La Nature*, 1895, **52**, 544).—A number of seeds were kept for 15 years in various gases. Seeds of lucerne, wheat, vetch, and coriander completely lost the power of germinating when kept in hydrogen, which was probably not absolutely dry. The following percentage of lucerne seeds germinated after being kept in the different gases. In oxygen, 0·68 per cent.; nitrogen, 56·56; chlorine and hydrogen chloride, 6·2; hydrogen sulphide, 0·99;

hydrogen arsenide, 70·98 and 68·82; carbonic oxide, 84·2; nitrogen peroxide, 0·97 and 0·62 per cent. None of the seeds kept in carbonic anhydride germinated, possibly owing to the presence of too much moisture.

After being kept in different alcoholic solutions, the following amounts of lucerne seed germinated: alcohol, alone 66·6 per cent.; concentrated solution of mercuric chloride, 20·2; sulphurous acid, 0·15; hydrogen sulphide, 7·03; nitrogen peroxide, 4·16. In alcoholic solutions of chloroform and phenol, all the seeds were destroyed. Many of the seeds which germinated were planted, and produced normal plants.

If the gases and the seeds had been more thoroughly dried, more of them would probably have retained their vitality. N. H. J. M.

**Nitrogen Assimilation in the Cotton Plant.** By CHARLES E. COATES and W. R. DODSON (*Journ. Amer. Chem. Soc.*, 1896, 18, 425—428).—Experiments were made to ascertain whether the cotton plant, which, like the *Leguminosæ*, is highly nitrogenous, can assimilate free nitrogen.

The plants were grown in pots each containing about 6 lbs. of ignited white sand, with and without minerals. Pots 1—2 had nothing added; pots 3—4 had mineral food; pots 5—7 had minerals, and, in addition, 25 c.c. of soil extract (from cotton soil, and containing in 25 c.c. N = 0·0003 gram).

In pots 1, 2, and 3, the plants died in three or four weeks, apparently from nitrogen starvation. The plant of pot 4 stopped growing after about six and a half weeks and lived two weeks longer, when it was taken up; the plants of pots 5 and 6 were taken up at the same time, having stopped growing. The following analytical results show that, under the conditions of the experiments, there was no fixation of nitrogen, either with or without soil extract, the slight gain being within the limits of experimental error. The results are in grams:

| | Pot 4. | Pot 5. | Pot 6. | Pot 7. |
|---|---|---|---|---|
| Nitrogen in seed sown… ………. | 0·004 | 0·0038 | 0·0039 | 0·0036 |
| Nitrogen found in seed (? in total produce *) …………………… | 0·0068 | 0·0056 | 0·0074 | 0·0080 |
| Dry matter in seed (? in total produce) ………………………… | 0·5050 | 0·4768 | 0·8350 | 0·9664 |

N. H. J. M.

**Relation between the Transpiration of Plants and the Concentration of the Nutritive Solutions.** By B. HEINRICH (*Ann. Agron.*, 1897, 23, 186—187; from *Ber. Landw. Versuchs.-Stat. Rostock*, 1895, 2, 170).—In a damp atmosphere, oats evaporated 102 grams of water per gram of dry substance, whilst in dry air the water evaporated amounted to 618 grams.

In order to ascertain the effect of the concentration of nutritive solutions on evaporation, oats were grown in solutions containing different amounts of a mixture corresponding with the formula

* This would accord with the gain of nitrogen as given in the text: N = 0·0028, 0·0018, 0·0035, and 0·0044 gram.

$4HK_2PO_4 + CaCl_2 + 5Ca(NO_3)_2 + 2MgSO_4 + Fe_2Cl_6$. The following results were obtained :

| | | | | | |
|---|---|---|---|---|---|
| Strength of solution per cent. | 3 | 1 | 0·5 | 0·25 | 0·1 |
| Dry produce (grams) | 134 | 74 | 44 | 28 | 18 |
| Evaporation (c.c. per gram of dry produce) | 515 | 550 | 684 | 688 | 629 |

The evaporation increased up to the period of flowering, after which it diminished. The results recall those of Hellriegel (*Ann. Agron.*, **11**, 59), who showed that, according to the amount of calcium nitrate supplied, barley evaporated from 250 to 800 c.c. of water per gram of dry substance. (Compare also Dehérain, *ibid.*, **18**, 465.)

N. H. J. M.

**Migration of Calcium Phosphate in Plants.** By L. VAUDIN (*Ann. Agron.*, 1897, **23**, 232—233; from *Ann. Inst. Pasteur*, 1895, 636).—The results of previous experiments having shown that in presence of alkali malates, the sugars may keep calcium phosphate in solution, it seemed possible that the organic acids of plants may have a share in assisting the migration of calcium phosphate. The phosphoric acid of the stems of wheat accumulates in the seeds at the time of maturation, and migrates from the seeds, when they germinate, towards the organs in course of development.

An examination of aqueous extracts of wheat grain and ears at different periods, from the time when the ears formed (June 15) to the time of cutting, showed the presence of malic acid in the ears in June, succinic and malic acids in July, whilst in August the seeds contained a small amount of succinic acid, but no malic acid. The acidity (as $P_2O_5$) in June was 0·75, and in August 0·286 per cent. on the dry substance.

The dry grain contained 1·6 per cent. of sugar, and traces of succinic acid. During germination, starch is converted into sugar, and the succinic acid is replaced by malic acid. The calcium phosphate thus becomes soluble. When the sugars of the grain are converted into starch, succinic acid appears (produced, probably, from the malic acid, which disappears at the same time). During this period of maturation, the calcium phosphate becomes insoluble, owing to the decomposition of the solvents, sugar and malic acid; there is thus a simultaneous deposition of calcium phosphate and of starch.

Malic acid is found also in maize and barley at the time when the ears are formed; and, like wheat, ripe barley grains contain succinic acid. In leguminous plants, citric acid has the same *rôle* as malic acid in cereals.

N. H. J. M.

**Composition and Analysis of Wheats.** By AIMÉ GIRARD (*Compt. rend.*, 1897, **124**, 926—932).—Since the bye-products of the manufacture of flour are largely used as feeding stuffs for stock, it follows that the same general principles should be applied in their analysis as in that of the whole wheat and the flour (this vol., ii, 382). The chief point is to separate the nitrogenous constituents from the carbohydrates of the woody fibre, but at present no process is known which permits this to be done completely and accurately. In order to separate the starch from the integuments, &c., of the seeds, the bye-

products are mixed with ten times their weight of ice-cold water, and subjected for 20 hours to the action of an agitator with paddles, the temperature being kept at 0°. The liquid is afterwards passed through a sieve, which arrests everything but the starch and gluten. The latter are dried and weighed, and afterwards separated in the manner previously described (*loc. cit.*). If this separation is found to be difficult owing to the physical condition of the gluten, it should be mixed with a definite quantity of flour from the same wheat, the proportions of starch and gluten in which have already been determined.

In order to determine the soluble matter, the best plan is to agitate the substance with ice-cold water, as in the determination of the starch and gluten, the liquid being filtered and the soluble matter determined in the filtrate. Agitation for 4 hours is sufficient.

When estimating the fat, it is advisable to adopt the plan recommended by the author some years ago, of treating the material with a 5 per cent. solution of hydrochloric acid, and again drying before treating with benzene. Since some of the fat is removed during the mechanical separation of the starch and gluten, a separate estimation of the fat in the residue is desirable. Indirect estimations of cellulose and the like are unsatisfactory, and it is better to make a direct determination of the nitrogenous and inorganic matter on the residue from which starch and gluten have been separated.

Analyses of the bye-products from four French wheats (*loc. cit.*) gave the following results: Water, 14·33 to 15·12. *Matter soluble in water*: proteids, 2·48—2·92; carbohydrates, 5·74—6·58; inorganic matter, 1·50—2·04. *Matter insoluble in water*: gluten, 4·31—4·78; starch, 26·36—29·79; nitrogenous woody matter, 4·88—6·52; fats, 2·68—3·65; celluloses, 29·06—31·38; inorganic matter, 1·81—2·12; loss, &c., 0·66—1·75 = 100.

The composition of the whole wheat was as follows: mean weight of a grain, 0·038 to 0·051 gram; kernel, 83·04 to 85·98; germ, 1·16 to 1·50; envelope, 12·52—15·61 = 100; water, 14·50—15·12; gluten, 6·64—7·13; soluble diastases, &c., 1·37—1·74; lignoses, 1·46—1·95; starch, 56·84—58·78; fats, 1·58—1·81; sugars, 0·75—1·33; galactin, 0·36—0·69; other soluble carbohydrates, 1·77—1·97; celluloses, 8·88—9·56; inorganic matter, 1·49—1·54; loss, &c., 0·74—1·94 = 100.

C. H. B.

**Physiological Study of the Cyclamen.** By ALEXANDRE HÉBERT and G. TRUFFAUT (*Bull. Soc. Chim.*, 1897, [iii], 15, 850—855).—A study of the changes of weight and composition produced in the different organs of the plant when grown in different kinds of soil.

M. W. T.

**Lime and Lupins.** By HEINRICH (*Bied. Centr.*, 1896, **26**, 231—232; from *Deut. landw. Presse*, 1896, No. 91, 809 and 816).—The results of the addition of 0·5, 1, 5 and 10 per cent. of chalk to sandy soil in which lupins were grown, showed that even the smallest amount was injurious to the plants, whilst with 10 per cent. the amount of dry produce was reduced from 150 grams to 27 grams. Gypsum (1 per cent.) reduced the produce to about half. Calcium phosphate (0·5 per cent.) was injurious, whilst in larger quantity (1 per cent.) it

completely destroyed the vegetation. Magnesium carbonate (0·5 per cent.) also killed the plants.

The injurious effect of calcium carbonate is to some extent diminished, but not eliminated, by the addition of kainite, or sodium nitrate. N. H. J. M.

**Mineral Constituents of the Watermelon.** By GEORGE F. PAYNE (*J. Amer. Chem. Soc.*, 1896, **18**, 1061—1063).—The watermelon contains about 0·3 per cent. of mineral matter, containing

| $SO_3$. | CaO. | MgO. | $K_2O$. | $Na_2O$. | $SiO_2$. | $P_2O_5$. | Cl. | $Fe_2O_3$. | Total. |
|---|---|---|---|---|---|---|---|---|---|
| 4·41 | 5·54 | 6·74 | 61·18 | 4·31 | 2·15 | 10·25 | 4·94 | 0·48 | 100. |

In selecting a suitable manure, the grower must pay particular attention to the amount of potash, which should largely exceed the phosphoric acid. L. DE K.

**Effect of Manure on the [Botanical] Composition of Crops.** By H. A. MORITZ FLEISCHER (*Bied. Centr.*, 1897, **26**, 161—164; from *Mitteil. Ver. Förd. Moorkultur in Deut. Reich.*, 1896, No. **23**, 441).—Whilst it is generally acknowledged that the application of nitrogenous manures to meadows induces an increased growth of the grasses, and, in consequence, a decrease of leguminous herbage, it is still uncertain what effect phosphoric acid, and potash, respectively have on the relation between the amount of *Gramineæ* and *Leguminosæ*. Maercker assumes that it is potash, and not phosphoric acid, which promotes the growth of leguminous plants rather than that of the grasses (Mentzel and von Lengercke's, *Landw. Kalender*, 1897, 69).

The results of experiments made on peaty land showed an increase in the percentage of *Leguminosæ* only after the simultaneous application of potash and phosphates, but it seems to be more important to apply large amounts of phosphoric acid than large amounts of potash. Whilst potash (150 kilos. per hectare) in conjunction with basic slag (50 and 100 kilos.) raised the percentage of leguminous herbage by 14·9 and 30·4 per cent. respectively, the percentage was increased by 28·29 after application of basic slag (100 kilos.) and potash (75 kilos.), and the addition of greater amounts of potash had no essential effect.

It is concluded that, on peaty soil, phosphoric acid is at least as important as potash in increasing the growth of the *Leguminosæ*, and that it must be of still greater importance in the case of ordinary mineral soils. The Rothamsted experiments, which Maercker quotes (*loc. cit.*) as supporting his view, do not include plots manured exclusively with potash. N. H. J. M.

NOTE.—Although there is no exclusively potash plot in the grass experiments at Rothamsted, the results of botanical separations of the herbage of plots receiving mineral manures, including and excluding potash, show conclusively that it is the potash and not the phosphoric acid to which increased growth of the *Leguminosæ* must be attributed. The following is a summary of results obtained in 1877 from a few plots :—Plot 3 (unmanured since 1856), plot 7 (complete minerals since

1856), plot 8 (complete minerals 1856—1861, but without potash since), and plot 4[1] (superphosphate 1859 and since).

| | Plot 3. | Plot 7. | Plot 8. | Plot 4[1]. |
|---|---|---|---|---|
| Gramineæ .............. | 71·75 | 74·38 | 81·19 | 71·78 |
| Leguminosæ ........... | 8·54 | 13·71 | 4·01 | 5·53 |
| Miscellaneous ......... | 20·31 | 11·91 | 14·80 | 22·69 |

N. H. J. M.

**Relative Manurial Value and the Preservation of the Nitrogen of Stable Manure.** By JULIUS H. AEBY, R. DORSCH, FR. MATZ and PAUL WAGNER (*Landw. Versuchs.-Stat.*, 1897, **48**, 247—360).—A large number of vegetation and other experiments are described from which the following conclusions are drawn. The nitrogen of stable manure is utilised to a considerably less extent than that of ammonia and nitrates, and to a less extent than that of green manure. Whilst the nitrogen of fæces and litter acts very slowly, the nitrogen of urine is very rapidly converted into ammonia, especially in presence of fæces, and the straw of cereals. The abundant application of fresh fæces immediately before sowing quickly growing plants, may give rise to diminished production owing to the liberation of free nitrogen which would otherwise be available to the plant. Destruction of nitrates is brought about by stable manure, as well as by fresh fæces, and even, although extremely slowly, by garden soil, by arable soil containing humus, and by the straw of cereals. The decomposition of nitrates by fæces is increased by addition of straw.

For every 100 parts of nitrogen in fæces and litter, stable manure receives not less than 100 parts of urine-nitrogen; in practice, however, stable manure does not usually contain more than 25 to 35, frequently only 10, parts of the urine-nitrogen for every 100 parts of fæces- and litter-nitrogen. This is owing to the separation of liquid manure, to loss as ammonia, and to elimination of free nitrogen.

Formation of ammonia in mixtures of fæces and straw is so slow that it need not be taken into account. When such mixtures are kept in layers of 80 to 100 cm. high, only slight changes take place during 12 months when it is trodden down. If turned over so as to admit air, decomposition takes place which may result in a loss of 50 per cent. of the organic matter. The usual preservatives (gypsum, superphosphate and kainite) mixed with the manure in the usual quantities have no effect on the process of humification.

As humification proceeds, the power of destroying nitrates diminishes, and it is probable that the better results obtained with rotten manure as compared with fresh manure is essentially connected with the diminished power of decomposing nitrates.

Carbon bisulphide applied to stable manure renders it unable to destroy nitrates, but the process is practically useless owing to the amount of bisulphide required and the length of time necessary for its action. Sulphuric acid and copper sulphate both act vigorously on the micro-organisms of stable manure, but it remains to be seen whether their use is practicable. N. H. J. M.

**Decompositions during the Putrefaction of Nitrogenous Organic Matter.** By F. W. THEODOR C. PFEIFFER, E. FRANKE, C.

GÖTZE and H. THURMANN (*Landw. Versuchs.-Stat.*, 1897, 48, 189—245).
—In the first series of experiments, the loss of nitrogen in cow's excrement (mixed with peat), both alone, and after admixture of gypsum, and of gypsum with superphosphate, respectively, was determined under the following conditions. (1) The manures were kept in two sets of flasks through both of which air was passed twice a week for five months, and through one of which air was passed continuously for five months longer. (2) The manures were kept in zinc boxes, (*a*) in a compressed and (*b*) in a loose state, for five months.

The next series of experiments were made to ascertain the effect of sulphuric acid (0·3 to 1 per cent.), superphosphate, potassium fluoride, and calcium hypochlorite respectively on the ammoniacal fermentation in solutions of urea, and of urea mixed with peat litter and liquid manure. The mixtures were kept for five months in bottles through which air was drawn continuously.

A third set of experiments was made to study the effect of lime and calcium carbonate on denitrification. Fresh horse-dung (100 grams), both alone and after addition of (1) lime (1 and 3 grams), (2) calcium carbonate (1 and 3 grams) respectively with a mixture of butyric, capric, and caproic acids (0·5 gram), and (3) sulphuric acid (0·5 gram), was kept for some weeks with 0·25 per cent. nitrate solution (1500 c.c.) in loosely stoppered bottles at the ordinary temperature, and the amount of nitrate determined from time to time.

In a fourth series, the amount of ammonia formed at the ordinary temperature, and at 30—32°, in peat saturated with urine and liquid manure, without further addition, and with addition of superphosphate, lime, calcium carbonate, and butyric acid, &c., respectively was determined. The manures were kept in bottles through which air was drawn continuously. The ammonia determinations were made at intervals of from two weeks to two months during the six months which the experiments lasted.

A series of pot experiments was made in which oats were grown in sandy soil (N = 0·062 per cent.), manured with potassium nitrate alone, with horse-, sheep- and cow-dung respectively, both alone and with addition of (1) potassium nitrate, (2) potassium nitrate and lime, (3) potassium nitrate and marl. The total produce and nitrogen in the produce were determined.

The following conclusions are drawn from the results of the various experiments:

Loss of nitrogen did not occur to any great extent when air has only limited access to the decomposing substance, but with increased and prolonged aëration as much as 42·6 per cent. of the total nitrogen was lost.

The effect of preservatives was uncertain. When used under conditions of vigorous aëration, the loss of nitrogen, although lessened, was nevertheless greater than the loss without preservatives and with less aëration. The mechanical treatment of manure is therefore of far greater importance than the use of chemical preservatives. In most of the experiments, the nitrogen lost was in the free state. Losses of ammonia were relatively slight.

The presence of lime (2 per cent.) prevented the denitrifying action

of fresh horse-dung on nitrate solution, whilst calcium carbonate (3 per cent.), and sulphuric acid (0·5 per cent.) had no effect. In vegetation experiments, 3 per cent. of lime, or 5 per cent. of marl, sufficed to limit the denitrifying action of cow-dung.

Oxidation of ammonia was only hindered by addition of sufficient superphosphate to completely combine with it. This result is, however, not opposed to the observed favourable effect of the addition of small quantities of superphosphate to manure, since in practice the oxidation of ammonia would be much less vigorous than in these experiments.

Addition of lime or calcium carbonate to decomposing manure at the ordinary temperature almost completely stopped the liberation of free nitrogen, and this gain exceeded the increased loss of ammonia. It is probable that loss of free nitrogen in stable manure might be diminished by layers of lime or marl, whilst loss through evolution of ammonia might possibly be to some extent hindered by covering the manure heap with soil.

Ammoniacal fermentation was rather increased than diminished by addition of large amounts of lime or superphosphate, and was only slightly hindered by 1 per cent. of sulphuric acid. N. H. J. M.

## Analytical Chemistry.

**Detection of Halogens in Organic Compounds.** By J. H. Kastle and W. A. Beatty (*Amer. Chem. J.*, 1897, **19**, 412—414).—About 0·1 gram of the substance to be examined is heated in a test-tube with about 0·5 gram of a mixture of silver and copper nitrates and a few drops of water until the nitrates are completely decomposed, the temperature not being allowed to rise above a dull red heat. Dilute sulphuric acid is added to the residue, and then zinc; after 5—10 minutes, the liquid is filtered, and tested with silver nitrate and nitric acid for the presence of halogens. If a volatile substance has to be examined, the tube employed is 6 × ¼ inches long, closed at one end, and divided into three roughly equal parts by two bends at right angles. About 0·25 gram of the substance is introduced into the closed end, and the tube is clamped with the limb next the open end pointing slightly upwards; about 0·5 gram of the dry, mixed nitrates is then introduced into the bend at the end of this limb, and the substance and nitrates are heated alternately (the former very gently) until all the substance has volatilised, and all the nitrates are decomposed; the residue is then examined as before. C. F. B.

**Estimation of Oxygen dissolved in Sea Water.** By Albert Lévy and Félix Marboutin (*Compt. rend.*, 1897, **124**, 959—961).—One of the authors described some time ago a method of estimating oxygen in natural waters by allowing it to oxidise a standard ferrous solution, the excess of ferrous salt being afterwards determined by means of permanganate solution. With spring or river water, the

results are identical with those obtained by extracting the gas as such, and they are the same whether permanganate or dichromate solution is used for the final titration. With sea-water, however, it is difficult to obtain accurate results with permanganate owing to the liberation of chlorine, but dichromate gives results identical with those obtained by the pump. Magnesium compounds do not interfere if the precipitate and liquid are thoroughly mixed. C. H. B.

**Estimation of Sulphur in Cast-Iron.** By FRANCIS C. PHILLIPS (*J. Amer. Chem. Soc.*, 1896, **18**, 1079—1086.)—About 1·5 gram of of the finely powdered and sifted metal is mixed with 8 grams of a mixture of 45 parts each of sodium dioxide and sodium nitrate, together with 10 parts of sodium carbonate; or 4 grams each of sodium nitrate and carbonate may be employed. On heating, a somewhat violent action occurs, and after 20 minutes the contents are fully oxidised. After cooling, the mass is softened in water, the solution decanted, and the residue ground, while wet, in a mortar. The solution and residue are then digested in a beaker on the water bath for 1 hour, after adding 2 c.c. of strong bromine water. The filtrate is acidified with hydrochloric acid, any silica is removed by evaporating to dryness, and the sulphuric acid is finally determined in the usual manner.

When testing ferromanganese, it is better to use a mixture of equal parts of sodium nitrate, and carbonate, omitting the sodium peroxide; under these circumstances, sodium manganate is not formed. Some grey irons cannot be crushed or ground; to these, the method is not applicable, but in their case the evolution method answers all requirements.

L. DE K.

**Optical Method for the Estimation of Sulphuric Acid.** By AGLOT (*Bull. Soc. Chim.*, 1897, [iii], **15**, 855—862).—This method depends on the opacity produced by the addition of barium chloride to a solution of sulphuric acid, as measured by means of an apparatus described by the author in another paper. Accurate results can only be obtained in alcoholic solution, impurities vitiate the results.

M. W. T.

**Modification of the Gunning Method for Nitrates.** By JOHN FIELDS (*J. Amer. Chem. Soc.*, 1896, **18**, 1102—1104).—From 0·7 to 3·5 grams of the sample is introduced into a 250—500 c.c. digestion flask, and 30 c.c. of sulphuric acid containing 1 gram of salicylic acid is added, and the whole gently heated to dissolve the nitrates; 6—7 grams of potassium sulphide is then added in small portions, the flask being well shaken after each addition. The heat is now rapidly increased until the mixture boils, and after the end of an hour the liquid is allowed to cool; it is then diluted, rendered alkaline, and the ammonia distilled off in the usual manner.

The chief advantage of the modification appears to be the short time of boiling and the obviation of frothing. L. DE K.

**Quantitative Separation of Arsenic and Antimony.** By OSCAR PILOTY and ALFRED STOCK (*Ber.*, 1897, **30**, 1649—1655).—The substance is placed in a round-bottomed flask of about 300 c.c. capacity,

and is then dissolved in 100 c.c. of concentrated hydrochloric acid, the flask is fitted up as if for steam distillation, except that the longer tube is provided with a T-piece at its upper extremity to allow of the introduction of both hydrogen chloride and hydrogen sulphide gases, and that the shorter tube is bent and passes into a receiver of about 600 c.c. capacity surrounded with ice. The contents of the round flask are heated to boiling, and a rapid stream of hydrogen chloride is passed through. When the whole apparatus has become filled with steam, the hydrogen sulphide is admitted at the rate of about two small bubbles per second. The distillation is continued until only a few c.c. of liquid remain in the flask, an operation which requires $\frac{1}{2}$—$\frac{3}{4}$ of an hour. All the arsenic is found in the receiver in the form of the trisulphide, mixed with free sulphur; it is collected, dissolved in as little dilute potash as possible, and then oxidised with bromine water, a slight excess of hydrochloric acid is added, and the contents of the flask briskly boiled until all traces of free bromine have disappeared. The clear hydrochloric acid solution is then heated at 70° for 3 hours while a stream of hydrogen sulphide is passed through, the gas is also kept passing through as the solutions cools, and the saturated solution is then put aside for 12 hours, when the arsenic pentasulphide may be collected on to a Gooch crucible, washed with water, absolute alcohol, pure carbon bisulphide, alcohol, and dry ether, then dried at 105° and weighed. The antimony may be estimated in the clear solution left in the round-bottomed flask by precipitating as sulphide, and treating in exactly the same way as the arsenic pentasulphide. The results are correct, and the complete operation occupies but 9 hours. It presents several advantages over E. Fischer's method (*Annalen*, 1881, **208**, 186), or the various modifications suggested by Hufschmidt, or by Classen and Ludwig (Abstr., 1885, 932). It is also much quicker than the method suggested by Friedheim and Michaelis (Abstr., 1895, ii, 415). J. J. S.

**Estimation of Carbon in Pig Iron.** By BERTRAND S. SUMMERS (*J. Amer. Chem. Soc.*, 1896, **18**, 1087—1091).—The old oxygen combustion process has never been excelled as regards accuracy, but with refractory residues the time required for a combustion may be about 3 hours, which renders the process unsuitable to works chemists.

The author has substituted a platinum tube for the usual porcelain or glass tube, and uses a specially constructed purifying and absorption apparatus, for details of which the original paper should be consulted. The chief characteristic is that rubber connections are avoided, the only rubber in use being at the ends of the combustion tube.

An analysis may be completed in something like 20 minutes.

L. DE K.

**Simplification of Organic Elementary Analysis.** By MAXIMILIANO DENNSTEDT (*Ber.*, 1897, **30**, 1590—1597).—The author's method of analysis admits of the simultaneous determination of carbon, hydrogen, sulphur, and halogen. The combustion tube is 83 cm. in length, and rests in an iron trough which is heated by Teclu burners, the usual form of combustion furnace being discarded. A layer of platinum black, 6—8 cm. long, occupies the middle of the tube, the

organic compound being weighed in a platinum or porcelain boat placed at a convenient distance from the metal; the usual form of apparatus for absorbing carbonic anhydride and water is attached to the end of the tube, and the combustion is carried out from the beginning in an atmosphere of oxygen. Supposing the substance to contain carbon, hydrogen, nitrogen, sulphur, and halogen, there are inserted between the platinum black and absorption apparatus four weighed boats, two of silver foil containing molecular silver, the others being of porcelain, and filled with lead peroxide. Then the increase in the weight of the silver boats is regarded as halogen and $SO_4$, whilst the lead peroxide boats take up $NO_2$ and $SO_2$; the lead peroxide must then be extracted with 33 per cent. alcohol to remove lead nitrate, the quantity of which is thereby determined. From these data the percentage of carbon, hydrogen, sulphur, and halogen may be calculated.

M. O. F.

**Ferrocyanides of Zinc and Manganese.** By EDMUND H. MILLER (*J. Amer. Chem. Soc.*, 1896, **18**, 1100—1102).—A preliminary note regarding the composition of metallic ferrocyanides. The author is of opinion that when titrating a zinc solution by means of potassium ferrocyanide, the precipitate does not consist of pure zinc ferrocyanide, but that it invariably contains potassium.

The pure compound can only be obtained by the direct action of hydrogen ferrocyanide on zinc oxide; the same is the case with manganese.

The author recommends a hydrochloric acid solution of platinic chloride as a very satisfactory indicator during the titration. It is used in the same way as uranium acetate, in a hot solution. The end reaction is a bright emerald-green which takes a few seconds to develop.

L. DE K.

**Estimation of Mercury.** By GEORGES DENIGÈS. (*Bull. Soc. Chim.*, 1897, [iii], **15**, 862—871).—To a solution containing any mercuric salt, a known quantity of potassium cyanide is added. After addition of ammonia and some potassium iodide, the mixture is titrated with decinormal silver nitrate solution, the appearance of silver iodide indicating the end of the reaction. The quantity of mercuric salt can be calculated from the equation: $2n\text{KCN} + m\text{HgX}'' + (n-m)\text{AgNO}_3 = m\text{Hg(CN)}_2 + \text{K}_2\text{X}'' + n - m\text{AgCN,KCN} + (n-m)\text{KNO}_3$. The reaction, as might be expected, is not quite complete, and consequently a correction must be applied to the results.

M. W. T.

**Microchemical Reaction for Didymium.** By FEDERICO CHAVES Y PÉREZ DEL PULGAR and FEDERICO RELIMPIO Y ORTEGA (*Anal. Soc. Españ. Hist. Nat.*, 1895, **24**, Actas 75—77).—The crystals obtained with potassium ferrocyanide in the method described by Behrens are figured and described; they consist of a hexagonal prism and basal plane with rounded faces, and are sometimes twinned. The optical characters conform with the hexagonal symmetry, and the birefringence is strong.

L. J. S.

**Separation of Manganese from Tungstic Acid; Estimation of Molybdenum.** By WALTER T. TAGGART and EDGAR F. SMITH (*J.

*Amer. Chem. Soc.*, 1896, **18**, 1053—1054).—The authors state that manganese chloride cannot be separated from sodium tungstate by means of yellow ammonium sulphide in the presence of ammonium chloride; no better results were obtained by using a solution of potassium carbonate. It is, however, probable that fusion with an alkali carbonate might be successful.

In the course of an analysis, molybdenum is often obtained as sulphide, which it is difficult to convert into a weighable form. The authors find that the dry sulphide, when ignited with anhydrous oxalic acid, rapidly burns to the pure trioxide. L. DE K.

**Separation of Vanadium from Arsenic.** By CHARLES FIELD and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1896, **18**, 1051—1052).—The authors have found that arsenic may be completely separated from vanadium by heating the mixed sulphides in a current of hydrogen chloride at a temperature not exceeding 250°.

The arsenic is completely volatilised, whilst the vanadium is left behind in the boat. The method, in addition to being satisfactory from an analytical point of view, certainly forms a very excellent means of freeing vanadium from arsenic. L. DE K.

**Metal Separations by means of Gaseous Hydrogen Chloride.** By J. BIRD MOYER (*J. Amer. Chem. Soc.*, 1896, **18**, 1029—1044).—The author calls attention to the use of gaseous hydrogen chloride in analysis. The most convenient way of preparing it is to drop sulphuric acid from a tap funnel into strong hydrochloric acid contained in a 3-litre flask. The gas is then dried by passing it through two wash bottles containing sulphuric acid, and finally through a calcium chloride tower. The substance to be acted on is weighed out in a porcelain boat, and the latter is placed in a combustion tube made of hard glass.

The oxides of antimony, bismuth, and arsenic are completely volatilised as chlorides at a temperature varying from 130° to 180°, whilst those of lead, copper, cadmium, zinc, silver, nickel, and copper are not volatilised at that temperature, so that their chlorides remain in the boat and may be weighed. Copper oxide is, however, but superficially acted on, and, if it is mixed with bismuth oxide, it should be dissolved in a little hydrochloric acid before heating it in the current of hydrogen chloride to volatilise the bismuth.

The process is, therefore, a very convenient one for the separation of antimony, arsenic, or bismuth from any of the others. When iron is present it cannot be employed, as it is very difficult to prevent the volatilisation of a little ferric chloride. The only drawback seems to be the very long time (average 7 hours) necessary to expel the volatile chlorides. L. DE K.

**Solubility of Bismuth Sulphide in Alkali Sulphides.** By GEORGE C. STONE (*J. Amer. Chem. Soc.*, 1896, **18**, 1091).—Stillman (this vol., ii, 127) has proved that when a solution of a bismuth salt is neutralised with aqueous soda and then heated with excess of sodium sulphide, a considerable amount of bismuth sulphide dissolves in that reagent.

The author confirms this statement, but he also finds that bismuth sulphide precipitated from an acid solution by means of hydrogen sulphide is not soluble when heated with excess of an alkali sulphide.

L. DE K.

**Separation of Bismuth from Lead.** By ARTHUR L. BENKERT and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1896, **18**, 1055—1056).—The authors state that bismuth may be completely separated from lead by boiling the nearly neutralised solution with excess of a solution of sodium formate containing a little formic acid. The precipitate contains a little lead from which it may be completely freed by redissolving in nitric acid and precipitating a second time. The basic bismuth formate thus obtained is then dissolved in dilute nitric acid, and precipitated as usual with ammonium carbonate. L. DE K.

**Quantitative Testing of Ethereal Oils.** By SCHIMMEL AND CO. (*Chem. Centr.*, 1896, ii, 977—978; from Schimmel and Co.'s *Bericht*, 1896, October. Compare Abstr., 1895, ii, 333—540).—Bergamot oil has a sp. gr. = 0·882—0·886 at 15°, and a rotatory power = +8° to +20° at 15—20° (100 mm. tube). The specific gravity is reduced by adulteration with turpentine oil, citron oil, orange oil, alcohol, and distilled bergamot oil, whilst fatty oils, cedar-wood oil and gurjun balsam oil increase it. The pure oil dissolves in half a part or more of 90 per cent. alcohol, but 80 per cent. alcohol does not form a clear solution with all oils, probably owing to the presence of wax-like substances introduced into the oil by pressing the rind. The residue after evaporation amounts to 5—6 per cent., and consists mostly of bergaptene; more than 6 per cent. residue indicates the presence of fatty oil. The essential constituent of the oil is linalylic acetate, $C_{10}H_{17}OAc$, which amounts to 30—40 per cent. This is determined by boiling 2 grams of oil with 10 c.c. of semi-normal alcoholic potassium hydroxide solution for half an hour and determining the excess of alkali in the cold solution after addition of water by means of semi-normal sulphuric acid, using phenolphthalein as indicator. The percentage of acetate $x$ is formed from the formula $x = g \div 19{\cdot}6\frac{y}{2}$, where $y$ is the number of c.c. of alkali used and $g$ the weight of oil taken.

Oil of lemon has a sp. gr. = 0·858—0·861 at 15°, and the rotatory power at 20° = +59° to +67°, usually only 64° (the difference in the angle of rotation at temperatures from 10—20°, for 1° = −9′, from 20—30° = −8·2°). Adulteration with turpentine oil alone is easily detected by the decreased rotation. The presence of orange oil with turpentine oil may be proved by slow distillation, when the first distillate which contains the pinene of boiling point lower than that of limonene, possesses a considerably lower rotatory power than that of the original oil.

Orange oil has a sp. gr. = 0·848—0·852 at 15°, and a rotatory power at 20° = +96° to +98° (100 mm. tube). All adulterants, such as turpentine oil, alcohol, and oil of lemon, cause a considerable reduction of rotatory power. Turpentine oil may be recognised by the same method as that used in the case of oil of lemon.

Lavender oil has a sp. gr. = 0·883—0·895 at 15°, and the rotatory power at 20° = −4° to −8° (100 mm. tube). The pure oil forms a

clear solution in three times its volume and more of 70 per cent. alcohol. Linalylic acetate with some geranylic acetate is the main constituent of the oil. The former is determined as in the case of bergamot oil, and should amount at least to 30 per cent.; very good oils contain 40 per cent. and more.

In oil of cloves, methylic alcohol and furfuraldehyde have been detected; the latter is perhaps the cause of the darkening of various ethereal oils.

In American peppermint oil, amylic alcohol and small quantities of sulphur compounds, probably for the most part dimethylic sulphide, were detected.

Oil of rue has a sp. gr. $=0{\cdot}833$—$0{\cdot}840$, and a rotatory power $=+0^\circ\ 13'$ to $+2^\circ\ 10'$ (100 mm. tube). The pure oil forms a clear solution in 70 per cent. alcohol, and solidifies at 8—10° in consequence of the separation of its main constituent, methyl nonyl ketone.

French or Italian oil of rosemary has a sp. gr. of more than 0·900, and a slight dextrorotatory power. The pure oil forms a clear solution in half a part and more of 90 per cent. alcohol, as also in 10 parts of 80 per cent. alcohol. E. W. W.

**Chemico-legal Detection of Alkaloids and Narcotic Substances.** By ALBERT HILGER and K. JANSEN (*Zeit. anal. Chem.*, 1897, **36**, 344—346; from *Forschungsber. über Lebensmittel*, 1, 14, 30).—The authors have applied the method of Küster (*Zeit. anal. Chem.*, **29**, 118) to the separation of the above substances. The method consists in treating the material to be examined with alcoholic tartaric acid, evaporating the filtered extract with plaster of Paris, and extracting the powdered mass, first in an acid condition, and then after making alkaline, with ether and with chloroform in a Soxhlet extractor.

Strychnine is not extracted by ether, whether acid or alkaline. Chloroform extracts notable proportions from the acid mass, but the greater part after rendering alkaline. When strychnine or brucine has been mixed with decomposed animal matter, the ethereal extracts contain only ptomaines. When potato or beer is present, the ethereal extract from the acid mass will contain solanidine or hop-resin, the alkaline ether extract, and the chloroform extracts contain the alkaloids.

From animal and vegetable matters mixed with atropine, the acid ether extracts only traces of the alkaloid; the acid chloroform extracts the bulk of the atropine. The alkaline extracts contain only traces.

Veratrine is extracted by both solvents, from both acid and alkaline masses, but chloroform is the better solvent.

Colchicine and digitalin are best extracted by chloroform after making alkaline, although traces are extracted in the other three cases.

Morphine is not extracted by either solvent from an acid mass, but both solvents, as well as amylic alcohol, remove it from the alkaline mass.

The extracts containing the alkaloids are as a rule colourless.

M. J. S.

# General and Physical Chemistry.

**Chemical Action of Light.** By JOHN GIBSON (*Zeit. physikal. Chem.*, 1897, **23**, 349—354).—The author contends that in all cases the chemical action of light is such that the new products have a higher conductivity than the original. Thus the effects on selenium, sulphur, phosphorus, and mercuric sulphide are all of this nature. By the combination of hydrogen and chlorine, and the decomposition of silver and mercury salts, the resulting products have increased conductivity. Under the influence of light, lead oxide changes to the peroxide, and manganous hydrate oxidises, in each case with increase of conductivity. The action on solutions of chlorine, potassium iodide, and bromine is of the same nature, but an apparent exception is found in the case of nitric acid, which is decomposed by light. This is, however, not an exception, as the conductivity of nitric acid solutions increases up to 32 per cent., when the maximum is reached, whilst the decomposition by light ceases when the concentration has fallen to 47 per cent. Other examples are also given, but the author points out that this simple and general law may be masked by secondary reactions between the products initially formed.

L. M. J.

**Action of Light on Gaseous Mixtures, with Special Reference to Hydrogen and Chlorine.** By ARMAND GAUTIER and H. HÉLIER (*Compt. rend.*, 1897, **124**, 1128—1133).—The experiments were made with pure hydrogen prepared in the usual way, and chlorine prepared by the action of hydrochloric acid on manganese peroxide precipitated by dilute nitric acid from solutions of the (?) "bichloride." Whether dry or moist, the two gases do not combine in the dark, no matter how long they may remain in contact.

Direct experiments showed that practically no combination of the two gases takes place under the influence of the light of a candle equivalent to 0·1 of a carcel, and placed at a distance of 1 metre, and only traces of hydrogen chloride are formed even after exposure to this light for several days, provided the gases are pure and dry.

C. H. B.

**Isomerism of Position and Rotatory Power.** By PHILIPPE A. GUYE (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1157—1160).—From the results of Frankland and Wharton (Trans., 1896, 1309 and 1583) and others, it appears that para- derivatives are more active than meta-, and meta- more active than ortho-. This result is in harmony with the relative position of the centre of gravity in the several groups, but, as the author points out, the variation of the product of asymmetry might occur in such a manner that the ortho-compound would exhibit the greatest, and the para-compound the smallest activity. From the relative position of the centre of gravity in the different groups, it might be inferred that a compound containing the phenyl group would have a greater or smaller rotatory power than a compound containing the tolyl group. This is, however, not always the case, as the phenyl

derivative sometimes occupies an intermediate position among the three tolyl derivatives, showing that the constitution as well as the mass of a substituting group influences the rotation. H. C.

**Two Methods for the Measurement of the Dielectric Constant and Electrical Absorption with Rapid Vibrations.** By PAUL DRUDE (*Zeit. physikal. Chem.*, 1897, **23**, 267—325).—The more rapid vibrations are more convenient than the ordinary slower discharges owing to their applicability in the case of conductors. The method first described consists of the determination of the ratio of the wave-length in air and in the liquid examined. An ordinary form of Hertzian oscillator is employed, and the position of the nodes determined (1) when the wires are in air, (2) when they pass through a trough of the liquid. For non-absorbing liquids, the dielectric constant is given by the square of this ratio, in the case of absorbing liquids by $r^2(1-a^2)$ where $a$ is the absorption coefficient. For conductors, the absorption coefficient can be calculated from the conductivity, but in the case of liquids showing anomalous absorption, that is, which absorb, but do not conduct, the absorption was determined by the preparation of aqueous solutions of equal absorbing power, as shown by the number of nodes observable. In the second method, condensers, filled with (1) air, (2) the compound required, were, by means of an adjustable length of wire, brought into resonance with the oscillator and their capacities, and in this way the dielectric constant was determined. This method could also be employed for solids, and is well adapted for finding the temperature coefficient, and for rare liquids. The results of the author for varying mixtures of methylic alcohol and water give a perfect, unbroken line, and thus differ from those obtained by Thwing, which exhibited many breaks. Unbroken or regular curves in close agreement with the numbers calculated by the mixture rule were obtained also for propionic acid and water, acetone and benzene, and acetone and water. A large number of liquids and solids were examined, and tables are given, but the results are frequently not in accord with those of other observers. This, however, is in many cases probably due to the difference in the wave-length, as experiments with acetaldehyde, benzaldehyde, acetone, and diethyl ketone show the variability of the dielectric constant with the wave-length, that is, measure the electric dispersion. The connection between the anomalous dispersion and chemical constitution is also discussed, the effect being apparently indicative of hydroxyl groups (see this vol., ii, 303).

L. M. J.

**Influence of Proximity of Substances on Voltaic Action.** By GEORGE GORE (*Phil. Mag.*, 1897, [v], **43**, 440—457).—The author has, on a previous occasion, shown that the difference of pressure due to gravity at the upper and lower ends of a vertical column of an electrolyte about 3 metres high, on two perfectly similar electrodes of the same metal at the upper and lower ends of the column, produced a very feeble current. If gravity, by producing pressure, exerts an extremely minute influence on chemical and voltaic action, similar effects, although excessively minute ones, must be produced by the gravitative action of a large mass of metal or other substance on a

voltaic electrode at the end of a horizontal column of electrolyte presented to it. Experiments confirming this view are described in the paper. H. C.

**Effect of Great Current-strength on the Conductivity of Electrolytes.** By THEODORE W. RICHARDS and JOHN TROWBRIDGE (*Phil. Mag.*, 1897, [v], **43**, 376—378).—As the authors' method of determining resistance by measuring its damping effect on electric oscillations applies to electrolytes, provided that the resistance to be measured is less than 20 ohms, experiments were made to ascertain whether the intense current involved in the discharge of a large condenser is capable of causing any change in the condition of an electrolyte. It was found that the resistance of concentrated copper sulphate and zinc sulphate solutions is not essentially altered by great alterations in the strength of the current. That the strong instantaneous current, which alters so much the resistance of gases, has so little effect on solutions, is no doubt due to the great mass and specific heat of the material, which must be warmed in the latter case. H. C.

**Thermo-electric Properties of some Liquid Metals.** By WILLIAM BECKIT BURNIE (*Phil. Mag.*, 1897, [v], **43**, 397—410).—Tin, lead, bismuth, and mercury were each thermo-electrically compared with copper, the tested metal being contained in a hard glass tube, so that the observations could be pushed to temperatures considerably above those of the melting metals, and the changes in the thermo-electric properties during the process of melting observed. About the melting point, a small variation of temperature produces a considerable change in the direction of the thermo-electric curve. The effect is smallest with lead, with tin it is larger, and with bismuth it is very remarkable, that metal changing during melting from an exceedingly active thermo-electric metal to one very similar to lead in its thermo-electric properties. With mercury, also, a great change takes place at the melting point. H. C.

**Heats of Vaporisation of Liquids.** By S. ROSLINGTON MILNER (*Phil. Mag.*, 1897, [v] **43**, 291—304).—The author shows that the internal heat of vaporisation of a liquid may be expressed by the formula, $L_i = \frac{RT}{JM}\left\{\frac{1}{0{\cdot}4343}\log_{10}\frac{v'-b}{v-b} + \frac{b}{v-b} - \frac{b}{v'-b}\right\}$ in which $v$ and $v'$ are the specific volumes of the liquid and saturated vapour respectively. The quantity $b$, although not constant, has a value satisfying van der Waals's equation, $(p + a/v^2)(v - b) = RT/M$, $v$ being the volume of the liquid and $a$ an absolute constant. H. C.

**Dynamics of Homogeneous Endothermic and Exothermic Chemical Reactions.** By MICHEL PETROVITCH (*Compt. rend.*, 1897, **124**, 1344—1346).—A calculation of approximate relationships between temperature, time, and the masses of reacting substances in any homogeneous system in which chemical changes are taking place.

H. C.

**Gradual Change and Thermodynamics.** By PIERRE DUHEM (*Zeit. physikal. Chem.*, 1897, **23**, 193—266).—The author investigates

at considerable length the thermodynamical equations applicable to the case of the slow alteration of a substance which tends to reach a final natural state. Such a slow change is well illustrated in the case of sulphur, for which the freezing point is a maximum when the sulphur is previously kept at a temperature of 121°. On the assumption that the melted sulphur gradually changes to a modification containing the element in two states, and that the freezing point depends on the ratio of these, the author applies his previous thermodynamical deductions to the sulphur changes. The velocity of solidification of overcooled melted sulphur at any particular temperature varies according to its previous history, and the dependence of this velocity on (1) the temperature of the melted sulphur, (2) the time during which it was kept at this temperature, and (3) the time of overcooling are all proved to be in accord with the theoretical deductions. The velocity of the change from monoclinic to rhombic sulphur is, in a similar manner, dependent on the previous history, and the results are again found to be in accord with the theory. The changes in monoclinic sulphur when kept for a long time at the ordinary temperature and the effect of repeated crystallisations are considered, and also the slow changes of rhombic sulphur at different temperatures and the effect of repeated melting and solidification. The author finally investigates the cyclical change by which the sulphur finally returns to its original state, and shows that in this case the well known Clausius inequality holds good.

L. M. J.

**Reduction of the Freezing Point of an Aqueous Solution.** By A. Ponsot (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1073—1078. Compare Abstr., 1896, ii, 636.)—The author describes the ideal conditions which should be as far as possible maintained in determining the freezing points of dilute solutions, the prevention of any loss of heat by radiation from the solution being one of the most important. He criticises Raoult's conclusions on this subject.

H. C.

**Means of Recognising a Good Method of Cryoscopy.** By A. Ponsot (*Compt. rend.*, 1897, **124**, 1227—1230).—A mathematical discussion of the influence of superfusion on determinations of the freezing points of solutions, and the correction thereby rendered necessary.

C. H. B.

**Heat of Formation of Zinc Hydroxide.** By Gustave Massol (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1104—1105).—Since

$$C_3H_4O_2 + ZnO \text{ sol.} = +15{\cdot}37 \text{ Cal.}$$
$$C_3H_4O_2 + Zn(OH)_2 \text{ sol.} = +11{\cdot}05 \text{ Cal.}$$

and the heat of fusion of $H_2O = -1{\cdot}43$ Cal., it follows that

$$ZnO \text{ sol.} + H_2O \text{ sol.} = Zn(OH)_2 \text{ sol.} + 2{\cdot}89 \text{ Cal.}$$

The heat of hydration of zinc oxide is therefore exothermic, as is the case with most other oxides.

J. J. S.

**Thermochemistry of the Sodioacetylenes.** By Camille Matignon (*Compt. rend.*, 1897, **124**, 1026—1028).—The violent action of water on the sodioacetylenes was regulated by placing the compressed substance in a small inverted glass vessel which was immersed in the

calorimeter. In some experiments, the sodioacetylene was decomposed by dilute hydrochloric acid and in others by water.

$C_2HNa$ sol. + HCl diss. = $C_2H_2$ gas + NaCl diss. develops + 28·3 Cal.
$C_2HNa$ sol. + $H_2O$ = $C_2H_2$ gas + NaOH diss. develops + 14·5 Cal.

and it follows that

$C_2$(diamond) + H + Na sol. = $C_2HNa$ sol. absorbs − 29·2 Cal.

Further:

$C_2Na_2$ sol. + 2HCl diss. = $C_2H_2$ gas + 2NaCl diss. develops + 64·96 Cal.
$C_2Na_2$ sol. + $2H_2O$ = $C_2H_2$ gas + 2NaOH diss. develops + 37·6 Cal.

and hence

$C_2$(diamond) + $Na_2$ sol. = $C_2Na_2$ sol. absorbs − 8·8 Cal.

It follows that

$C_2H_2$ gas + Na = $C_2NaH$ sol. + H develops + 28·9 Cal.
$C_2H_2$ gas + $Na_2$ = $C_2Na_2$ sol. + $H_2$ develops + 49·3 Cal.

The thermal value of the first hydrogen is comparable with that of the alcoholic function of the tertiary alcohols; the value of the second hydrogen is distinctly lower.

Both the sodium derivatives are endothermic and retain part of the energy of the acetylene molecule, which they resemble in decomposing with liberation of carbon when their temperature is raised rapidly. When pure, they can be handled without danger, and are not sensitive to percussion or friction, but if mixed with oxidising agents they become violently explosive and as a rule are sensitive to friction.

C. H. B.

**Heat of Formation of Sodioacetylenes.** By ROBERT DE FORCRAND (*Compt. rend.*, 1897, **124**, 1153—1155).—If Matignon's results (preceding abstract) are recalculated with + 43·08 Cal. as the value of the reaction Na + Aq, the numbers + 28·58, + 48·56, and + 19·98 are obtained instead of those given by Matignon (+ 28·9, + 49·3, and + 20·4) who probably took Na + Aq = + 43·45 Cal.

Matignon's conclusion that the thermal value of the first displaceable hydrogen approximates to that of tertiary alcohols, can only be arrived at if the heat of solidification of the acetylene is neglected. From Villard's results on the heats of formation of hydrates of gases, and the known heat of solidification of carbonic anhydride, it seems very probable that the heat of solidification of acetylene is about + 6·54 Cal., and if this value is adopted, the following results are obtained:

| | | |
|---|---|---|
| $C_2H_2$ sol. + Na sol. = $C_2HNa$ sol. + H gas | develops | + 22·04 Cal. |
| $C_2H_2$ sol. + $Na_2$ sol. = $C_2Na_2$ sol. + H gas | ,, | + 42·02 Cal. |
| $C_2HNa$ sol. + Na sol. = $C_2Na_2$ sol. + H gas | ,, | + 19·98 Cal. |
| $\frac{1}{2}C_2H_2$ sol. + Na sol. = $\frac{1}{2}C_2Na_2$ sol. + H gas | ,, | + 21·01 Cal. |

It is clear that, when calculated on this basis, the thermal value of the first hydrogen is considerably less than that of tertiary alcohols. At the same time, it is also clear that the difference between the first and second hydrogen is much greater than can be attributed to experimental errors, but many analogous cases are known. C. H. B.

**Calculation of the Calorific Power of Coals by Dulong's Law.** By GEORGES ARTH (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1112—1116. Compare *ibid.*, 1895, [iii], **13**, 820).—The author has examined 13 specimens of coal from *Bascoup* (*ibid.*, [iii], **7**, 478) and finds that in each case the calorific power as determined by experiment agrees with that deduced from Dulong's formula. J. J. S.

**Calculation of the Coefficient of Expansion of Gases based on a Theory of Valency.** By JOACHIM SPERBER (*Zeit. anorg. Chem.*, 1897, **14**, 374—378).—The author makes use of his theory of valency (this vol., ii., 307) for the purpose of calculating the coefficient of expansion of certain diatomic gases. In this way, the coefficients of expansion of fluorine, chlorine, bromine, and oxygen are found to give values that differ but slightly from 0·00365. H. C.

**Variation of the Dissociation Coefficient with Temperature.** By S. ROSLINGTON MILNER (*Phil. Mag.*, 1897, [v], **43**, 286—290).—A proof of the law of the variation of the dissociation coefficient with temperature, first worked out by van't Hoff. H. C.

**Non-concentrating Solutions.** By WILHELM MEYERHOFFER (*Ber.*, 1897, **30**, 1810—1812).—Certain solutions in contact with the dissolving substance undergo no further concentration on evaporation, but if water is removed from the system at all, this water is lost by the solid salt and not by the solution. This is the case with any solution in contact with ice, and in many systems in which an aqueous solution is in contact with a hydrated salt. In the latter case, if the solutions are saturated, they form points on a curve connecting two multiple points of different order, a triple point with a quadruple point, or a quadruple point with a quintuple. Such curves have a temperature maximum in the lower multiple point. H. C.

**Solubilities of Several Readily Soluble Salts.** By FRANZ MYLIUS and ROBERT FUNK (*Ber.*, 1897, **30**, 1716—1725).—The authors have determined the solubilities of several readily soluble salts which had hitherto not been studied. The results are correct to 1 per cent. The finely divided salt was shaken with water at 18° for at least an hour, the excess of salt was allowed to subside at the same temperature, and a portion of the clear solution was removed by a pipette, weighed, and analysed.

In the Table, *a* gives the most stable form of the compound in the presence of the solution at 18°. The molecules of salts of lithium, sodium, and potassium, with monobasic acids, are doubled in order that the numbers in column *e* may be comparable, *b* gives the sp. gr. of the saturated solutions, *c* the percentage of anhydrous salt in the solution, *d* the amount of salt in grams dissolved in 100 grams of water, and *e* the number of molecules of water to one molecule of anhydrous salt in the solution, *f* gives the melting point of the salt of the formula given in the first column, *g* gives the number of molecules of water required to dissolve one molecule of the salt, and *h* the water of crystallisation expressed as percentage of the water required for solution.

Magnesium iodate occurs in the anhydrous form and also crystal-

| — | — | a. | b. | c. | d. | e. | f. | g. | h. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Lithium chlorate | $(LiClO_3)_2$ | 1·815 | 75·8 | 313·5 | 3·2 | 125° | 3·2 | 0 |
| 2 | Calcium chlorate | $Ca(ClO_3)_2 + 2H_2O$ | 1·729 | 64 | 177·8 | 6·5 | part under 100° | 4·5 | 31 |
| 3 | Lithium chromate | $Li_2CrO_4 + 2H_2O$ | 1·574 | 52·6 | 110·9 | 6·7 | about 185° | 4·7 | 30 |
| 4 | Zinc chlorate | $Zn(ClO_3)_2 + 6H_2O$ | 1·914 | 65 | 186·2 | 7 | 60° | 1 | 87 |
| 5 | Potassium fluoride | $(KF)_2 + 4H_2O$ | 1·502 | 48 | 92·3 | 7 | about 46° | 3 | 57 |
| 6 | Calcium nitrate | $Ca(NO_3)_2 + 4H_2O$ | 1·548 | 54·8 | 121·2 | 7·4 | 44° | 3·4 | 54 |
| 7 | Magnesium chlorate | $Mg(ClO_3)_2 + 6H_2O$ | 1·594 | 56·3 | 128·6 | 8·2 | 40° | 2·2 | 74 |
| 8 | Zinc nitrate | $Zn(NO_3)_2 + 6H_2O$ | 1·664 | 53·9 | 116·9 | 9 | 36·4° | 3 | 67 |
| 9 | Strontium chlorate | $Sr(ClO_3)_2$ | 1·839 | 63·6 | 174·9 | 9·3 | does not melt. | 9·3 | 0 |
| 10 | Lithium bromate | $(LiBrO_3)_2$ | 1·833 | 60·4 | 153·7 | 9·8 | ,, | 9·8 | 0 |
| 11 | Magnesium bromide | $MgBr_2 + 6H_2O$ | 1·655 | 50·8 | 103·4 | 9·9 | about 165° | 3·9 | 61 |
| 12 | Magnesium iodide | $MgI_2 + 8H_2O$ | 1·909 | 59·7 | 148 | 10·4 | about 45° | 2·4 | 77 |
| 13 | Magnesium nitrate | $Mg(NO_3)_2 + 6H_2O$ | 1·384 | 43·1 | 75·7 | 10·8 | about 94° | 4·8 | 56 |
| 14 | Magnesium chromate | $MgCrO_4 + 7H_2O$ | 1·422 | 42 | 72·3 | 11 | part under 100° | 4 | 64 |
| 15 | Lead chlorate | $Pb(ClO_3)_2 + H_2O$ | 1·947 | 60·2 | 151·3 | 13·7 | does not melt. | 12·7 | 7·3 |
| 16 | Sodium chromate | $Na_2CrO_4 + 10H_2O$ | 1·409 | 38·1 | 61·4 | 14·6 | 24° | 4·6 | 69 |
| 17 | Lithium iodate | $(LiIO_3)_2$ | 1·568 | 44·6 | 80·3 | 25·2 | does not melt. | 25·2 | 0 |
| 18 | Sodium fluoride | $(NaF)_2$ | 1·044 | 4·3 | 4·4 | 104·8 | ,, | 105 | 0 |
| 19 | Magnesium iodate | $Mg(IO_3)_2 + 4H_2O$ | 1·078 | 6·44 | 6·88 | 292 | ,, | 288 | 1·4 |
| 20 | Calcium iodate | $Ca(IO_3)_2 + 6H_2O$ | 1 | 0·25 | 0·25 | 868 | ,, | 862 | 0·7 |
| 21 | Lithium fluoride | $(LiF)_2$ | 1·003 | 0·27 | 0·27 | 1038 | ,, | 1038 | 0 |

lised with $4H_2O$ when deposited by slowly cooling a warm saturated solution. A supersaturated solution, when cooled to 0° and well stirred, yields rhombic plates containing $10H_2O$. When a small quantity of this hydrate is warmed, it melts at 50° to a clear liquid; on cooling to 0°, the liquid becomes syrupy, but does not crystallise again unless rubbed with a glass rod. When the liquid is kept at 50° for several seconds, or for a longer time at the ordinary temperature, water is given up and crystals of the hydrate $Mg(IO_3)_2 + 4H_2O$ are deposited. The solubility of the hydrate $Mg(IO_3)_2 + 10H_2O$ increases rapidly with the temperature. A saturated solution at 0° contains but 3·1 per cent. of anhydrous salt, whereas a saturated solution at 50° contains 67·5 per cent.

The only hydrate of zinc iodate which could be obtained was $Zn(IO_3)_2 + 2H_2O$ which, according to Rammelsberg, requires 114 parts of water for solution.

The authors have obtained the hydrate $Ca(IO_3)_2 + 6H_2O$ described by Rammelsberg, but not the hydrate $Ca(IO_3)_2 + 4H_2O$ described by Ditte. When the hydrate $Ca(IO_3) + 6H_2O$ is suspended in water and the mixture heated to boiling, it is converted into the hydrate $Ca(IO_3)_2 + H_2O$.

Saturated solutions of the hydrate $Ca(IO_3)_2 + 6H_2O$ at

| | 0° | 10° | 18° | 30° | 40° | 50° | 54° | 60° |
|---|---|---|---|---|---|---|---|---|
| contain... | 0·1 | 0·17 | 0·25 | 0·42 | 0·61 | 0·89 | 1·04 | 1·36 |

per cent. anhydrous salt.

Saturated solutions of the hydrate $Ca(IO_3)_2 + H_2O$ at

| | 21° | 35° | 40° | 45° | 50° | 60° | 80° | 100° |
|---|---|---|---|---|---|---|---|---|
| contain... | 0·37 | 0·48 | 0·52 | 0·54 | 0·59 | 0·65 | 0·79 | 0·94 |

per cent. anhydrous salt. J. J. S.

**Influence of Water on the Solubility in Ether of Certain Compounds.** By HUGO SCHIFF (*Zeit. physikal. Chem.*, 1897, **23**, 355—356).—Phloretin is soluble in water to the extent of 0·12 per thousand and in ether to the extent of 4 per thousand. By the addition of 1 per cent. of water to the ether, the solubility increases to 50 per thousand and by saturation of the ether with water it again decreases to 35 per thousand. This increase by addition of water cannot be due to the formation of alcohol, in which phloretin is easily soluble, as the addition of 1 per cent. of alcohol to the ether only raises the solubility to 24 per thousand (compare Boedtker, this vol., ii, 367). L. M. J.

**Velocity of Solidification.** By GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1897, **23**, 326—328).—The velocity of solidification of overcooled sulphur and phosphorus was found by Gernez to be proportional to the overcooling. Experiments with salol, benzoic anhydride, benzophenone, diphenylamine, $\alpha$-naphthylamine, hydrocinnamic acid, and azobenzene, however, showed that, although the velocity is at first so proportionate, yet with further overcooling the velocity becomes constant. When the overcooling is so great that the heat developed by the solidification does not raise the temperature to the freezing point, the velocity again decreases greatly. This is the case for benzophenone for an overcooling of 90° and at a temperature of $-40°$; melted

benzophenone does not solidify when touched by a small portion of the solid, whilst if then slowly heated, solidification proceeds, but at first with very small velocity. For phosphorus, for which the heat developed by solidification is sufficient to raise the temperature 26°, the velocity of solidification at 0° is only 1/100 of the velocity at 24°, the lowest temperature investigated by Gernez. The maximum velocity is independent of the containing vessel, and is, the author states, a characteristic constant for each substance. L. M. J.

**Application of the Laws of Chemical Equilibrium to Complex Inorganic Compounds.** By WILHELM MEYERHOFFER (*Ber.*, 1897, **30**, 1804—1809).—Friedheim (Abstr., 1894, ii, 314) has prepared a number of complex inorganic compounds by the action of alkali phosphates or arsenates on chromates and sulphates. These compounds he regards, not as molecular compounds, but as formed of complex molecules of definite atomic structure. This view the author opposes in the present paper, showing that the formation of these compounds takes place under conditions precisely analogous to those which hold generally for the formation of those double salts which are usually regarded as molecular compounds. H. C.

**Precipitation of Organic Compounds by Bases.** By MARCEL LACHAUD (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1105—1108).—Dextrin is partially precipitated from its aqueous solutions by the addition of magnesia or any of the alkaline earth carbonates, but at the same time a part of the precipitating agent goes into solution. Similar results are obtained when solutions of such salts as aluminium sulphate, chrome alum, ferric sulphate or lead nitrate are added to a solution of dextrin and then rendered alkaline with ammonia. Extended experiments with dextrin, ferric sulphate, and ammonia showed that the whole of the dextrin can be precipitated if the ferric hydroxide is in large excess; if, however, the dextrin is in large excess, no precipitate is formed, and all the iron remains in solution. Many other organic compounds behave in much the same way as dextrin. J. J. S.

**Precipitation of Dextrin by Soils.** By MARCEL LACHAUD (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1108—1110).—The author finds that different vegetable soils are capable of precipitating dextrin from its solutions, and the same is true of gelatin solutions, but even to a greater extent. The amount precipitated is greater in the case of a barren soil or of a soil which has been calcined than with an ordinary fertile soil. J. J. S.

**Study of Capillary Affinity.** By MARCEL LACHAUD (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1110—1112).—Animal charcoal absorbs atmospheric moisture, the amount absorbed depending on the specimen of charcoal, and also on the temperature.

In the case of solutions, equilibrium is only slowly established if the charcoal is coarse and of compact texture; if, however, the charcoal is fine and light, equilibrium is established in 30—40 minutes. The chief factor in all cases of absorption is the strength of the solution. With mixtures of different solutions, the action of animal charcoal differs considerably according to the nature of the solutions; in most

cases, the charcoal exerts a selective absorbing action. Salicylic acid is absorbed more readily than any of its salts, and the absorption of the salts increases roughly with the molecular weight of the salt. It is impossible to give any exact method for estimating the values of animal charcoals. J. J. S.

**A New Laboratory Turbine.** By HEINRICH C. TRYLLER (*Ber.*, 1897, **30**, 1729—1731).—A turbine is described in which the ordinary form of propeller is replaced by a disc of iron wire gauze. The machine is more easily regulated, works more quietly, and requires less water than those constructed on the old principle. M. O. F.

**A New Extraction Apparatus.** By EMIL DIEPOLDER (*Ber.*, 1897, **30**, 1797—1798).—The new apparatus is an improvement on the form described by Schwarz (*Zeit. anal. Chem.*, 1884, **23**, 369). The vessel which contains the aqueous solution is a tall cylinder, and from the surface of the liquid the extracting agent is syphoned by means of a side-tube which leads into a distilling flask, the contents of which can be boiled. The vapour is then led to the condenser, from which the distillate passes to the bottom of the cylinder, and works up through the aqueous solution to the surface. Obviously, this form is applicable only in the case of specifically light extracting agents. When the liquid employed has a density greater than that of water, the syphon tube leads to the bottom of the cylinder, and the distillate is returned to the surface of the liquid.

A figure illustrates the proportions of the apparatus. M. O. F.

## Inorganic Chemistry.

**Liquefaction of Fluorine.** By HENRI MOISSAN and JAMES DEWAR (*Compt. rend.*, 1897, **124**, 1202—1205).—Fluorine under atmospheric pressure does not liquefy at $-183°$, the temperature of liquid oxygen boiling under atmospheric pressure, but if the pressure on the oxygen be reduced so that the temperature falls to about $-185°$, the fluorine condenses to a very mobile, yellowish liquid, the colour of which resembles that of a long column of the gas.

Fluorine at these low temperatures has no action on glass, and if silicon, boron, carbon, sulphur, phosphorus, or iron is cooled in liquid oxygen and then thrown into an atmosphere of fluorine, it does not take fire, nor is iodine displaced from iodides. Benzene and terebenthene, however, are decomposed with incandescence if the temperature exceeds $-180°$, and hence it would seem that the attraction of fluorine for hydrogen is the last to disappear at low temperatures.

When gaseous fluorine is passed into liquid oxygen, a white, flocculent precipitate forms rapidly, and if collected on a filter it deflagrates violently as soon as its temperature rises. This product is under investigation. C. H. B.

**Composition of Nitrogen Chloride.** By W. HENTSCHEL (*Ber.*, 1897, 30, 1792—1795).—The author's modification of Balard's method of preparing nitrogen chloride consists in mixing solutions of ammonium chloride and sodium hypochlorite, and extracting the product with benzene. If the quantity of ammonium chloride is limited, solutions of chlorine in nitrogen chloride are obtained, and are found to be of indefinite composition, but a homogeneous product is always formed if the molecular proportion of ammonium chloride to chlorine is equal to or greater than 2 : 3 ; the compound then has the normal composition, $NCl_3$, even if the proportion just indicated reaches 16 : 3.

A sketch of the apparatus employed for determining nitrogen in nitrogen chloride is given in the paper. M. O. F.

**Action of Water on Phosphoryl Chloride.** By J. ADOLPHE BESSON (*Compt. rend.*, 1897, 124, 1099—1102).—When a current of moist air is passed through phosphoryl chloride, metaphosphoryl and pyrophosphoryl chlorides are formed as well as phosphoric acids, and the same result follows when cold water is allowed to fall drop by drop into well cooled phosphoryl chloride. The products are difficult to isolate, but when distilled under very low pressure the residue consists of phosphoric acid and metaphosphoryl chloride, whilst the distillate consists of the pyrophosphoryl chloride mixed with some unaltered phosphoryl chloride. At 110°, pyrophosphoryl chloride decomposes into phosphoryl and metaphosphoryl chlorides, and the latter at a higher temperature splits up into phosphoryl chloride and phosphoric anhydride. Pyrophosphoryl chloride, $P_2O_3Cl_4$, does not solidify at $-50°$; it dissolves very rapidly in water with production of a slight turbidity which, however, disappears almost immediately. The regulated action of water on phosphoryl chloride yields pyrophosphoryl chloride, metaphosphoryl chloride, and phosphoric acid in proportions which vary with the conditions. The author has previously obtained, by the action of hydrogen sulphide on phosphoryl chloride, a compound, $P_2O_2SCl_4$, which is analogous to pyrophosphoryl chloride, $P_2O_3Cl_4$ (this vol., ii, 208). C. H. B.

**Graphite, Graphitite, and Graphitoid.** By ERNST WEINSCHENK (*Zeits. Kryst. Min.*, 1897, 28, 291—304. Compare Abstr., 1892, 406 ; 1893, ii, 320, &c.).—From a review of the evidence put forward for the existence of graphitite and graphitoid as distinct modifications or varieties of graphite, and from his own observations made on natural and artificial material, the author considers that there is no essential difference between these and graphite, and that they must therefore be taken as being identical with the latter.

The property of not swelling up when moistened with nitric acid and ignited, on which the name graphitite was based, is explained by the crystals of "graphitite" being smaller and more compact, and therefore freer from cleavage cracks into which the acid could penetrate. The so-called graphititic acid has been obtained in crystals having the outlines of the original graphitite, and with the same optical characters as graphitic acid. Graphitic acid has also been prepared from graphitoid. There is no difference between the readiness with which graphite and

graphitite burn, the rate of burning depending on the size of the scales and on the purity of the material. L. J. S.

**Purification of Commercial Potash and Soda.** By ERNST MURMANN (*Zeit. anal. Chem.*, 1897, 36, 379—380).—Potash and soda sold as "purified by alcohol" still contain traces of copper, lead, iron, alumina, and silica. The three former are best removed by cautiously treating the warm solution with hydrogen sulphide. An excess is easily avoided, or it may be afterwards removed by hydrogen peroxide. M. J. S.

**Lithium Borate.** By HENRI L. LE CHATELIER (*Compt. rend.*, 1897, 124, 1091—1094).—When boric acid and lithium carbonate are fused together in any proportions whatever, only one borate, $Li_2O,B_2O_3$, is obtained, and in this respect lithium is analogous to the alkali metals and differs from the metals of the calcium group. The salt crystallises in nacreous, triclinic lamellæ.

In presence of water, boric acid displaces the carbonic anhydride from lithium carbonate, and forms a salt which is analogous to borax, but which is so soluble in water that it could not be isolated.

When the anhydrous borate is dissolved in boiling water and the solution is allowed to cool, the salt, $Li_2O,B_2O_3 + 16H_2O$, is deposited in crystals which belong to the rhombic system; sp. gr. = 1·397 at 14·7°. Its heat of dissolution is $-28·4$ Cal. and the heat of hydration of the anhydrous salt, with formation of the solid hydrated salt, is $+43·4$ Cal. The action of lithium hydroxide (diss.) on boric anhydride (diss.) develops 9·8 Cal. for the first molecule of hydroxide and $9·3 \times 2$ Cals. for two molecules.

The hydrated salt melts completely in its water of crystallisation at 47°, and when heated until it becomes anhydrous there is no evidence of the formation of any intermediate hydrate.

The molecular reduction of the freezing point of the aqueous solutions is 100; the eutectic solution contains 0·6 per cent. of the anhydrous salt, and solidifies at $-0·6°$.

The solubility at first increases slowly with the temperature and then more and more rapidly as the melting point of the hydrated salt is approached. The crystallising point of solutions containing less water than the hydrated salt is 34°. The curve representing the solubility is continuous, but has a vertical tangent at the concentration corresponding with the composition of the hydrated salt, the phenomena being similar to those observed with calcium chloride, many mixtures of fused salts, and metallic alloys.

The crystallised salt effloresces when exposed to air, and absorbs small quantities of carbonic anhydride. C. H. B.

**Action of Hydrogen on Solutions of Silver Nitrate: Purification of Hydrogen.** By JEAN B. SENDERENS (*Bull. Soc. Chim.*, 1897, [iii], 15, 991—997).—Conflicting statements by previous investigators have led the author to study the behaviour of aqueous solutions of silver nitrate towards hydrogen. When the purified gas is passed through boiling solutions of the crystallised nitrate, heated in a reflux apparatus, the feebly alkaline action of the liquid is destroyed, and

the quantity of nitric acid produced, the weight of silver precipitated, and the velocity of the action, are found to be proportional to the concentration of the solution; they also increase with the duration of the experiment, but the relation is not in direct proportion, owing to the action of the nitric acid on the metal. Moderately rapid reduction takes place at 80°, the liquid, as in the case of boiling solutions, first becoming turbid and then gradually clear, a grey precipitate of silver being deposited; reduction proceeds still further if the liquid, filtered at this stage, is submitted to the action of the gas. Hydrogen also reduces cold solutions of silver nitrate, change being indicated by separation of metal and by the acidity exhibited by the liquid after treatment with the gas. As in the previous cases, the quantity of acid produced is proportional to the concentration of the solution.

The author's experiments were carried out with electrolytic hydrogen, and also with hydrogen from ordinary sources purified by passage through a concentrated sulphuric acid solution of potassium permanganate, a solution of this salt containing caustic potash, a tube containing cotton wool, a tube containing red-hot copper, and a flask of moderately concentrated silver nitrate. M. O. F.

**Alloys of the Silver-Copper Group.** By FLORIS OSMOND (*Compt. rend.*, 1897, **124**, 1094—1097).—The researches of various investigators on the melting points of silver-copper alloys indicate that these alloys, after solidification, are simple mixtures of the two metals, the alloy $Ag_3Cu_2$, described by Levol, being an eutectic mixture. Microscopic examination of a well-annealed button of Levol's alloy, under a sufficiently high power, shows that it is not homogeneous, as Behrens supposed, but has a structure identical with that of the perlite of steels. All other silver-copper alloys except those containing only very small quantities of one of the constituents consist, as the case may be, of yellow crystallites of copper, or white crystallites of silver, more or less completely enveloped in Levol's alloy. Microscopic examination, therefore, confirms the conclusions drawn from determinations of the melting points, and it may be taken that no definite compound $Ag_3Cu_2$ exists in these alloys. C. H. B.

**Silver-Copper Alloys.** By FLORIS OSMOND (*Compt. rend.*, 1897, **124**, 1234—1237).—The author has previously shown that alloys of silver and copper contain two constituents which have the appearance of the two metals, but since the properties of the alloys are very far from being the mean of those of their constituents, it would seem that the white and yellow components referred to cannot be simple metals.

Alloys were prepared containing 0·2, 0·5, 1·0, 2·0, and 4·0 per cent. of copper and silver respectively, and when examined quantitatively under the microscope it was found that in both cases part of the metal present in the smaller proportion was not recognisable as a distinct ingredient. Further experiments, in which the alloys were annealed at different temperatures, showed that the appearance of silver is not altered by the addition of 0·2 or 0·5 per cent. of copper, but with 1 per cent. of the latter it becomes recognisable as a separate constituent, and with 2 per cent. it is easily seen. Alloys of copper with

small quantities of silver behave similarly, and the silver becomes visible when the amount of it reaches 0·5 per cent.

These results seem to indicate a mutual solubility of solid copper and silver, as Matthiessen supposed, and this view is supported by the fact that when polished surfaces of silver and copper are placed in contact, and heated at 650—675° in an atmosphere of hydrogen, they adhere somewhat strongly, and the properties of the surface of each metal, after they have been separated, indicates that it contains a small quantity of the other, although the penetration extends only to a minute depth. C. H. B.

**Phosphorescent Strontium Sulphide.** By José Rodriguez Mourelo (*Compt. rend.*, 1897, **124**, 1024—1026 and 1237—1238).—Strontium sulphide prepared by reducing the pure sulphate with carbon is non-phosphorescent, but when strongly heated with starch it acquires feeble powers of phosphorescence. When prepared in a granular form by heating the commercial carbonate with sulphur, its phosphorescent properties are much more marked, and a still better product is obtained by heating the carbonate at a high temperature in a current of hydrogen sulphide, and afterwards heating the sulphide at very bright redness in an earthen crucible for 4 hours.

Following Verneuil's method for the preparation of calcium sulphide, strontium carbonate was moistened with a dilute solution of sodium carbonate and chloride, dried, converted into oxide, and heated with sulphur and a small quantity of basic bismuth nitrate. The product is much more intensely phosphorescent than any of those described above and the phosphorescence is readily excited.

The following method yields a sulphide which shows an extremely brilliant blue-green phosphorescence even under feeble excitation: 285 grams of ordinary strontium carbonate, 62 grams of flowers of sulphur, 4 grams of crystallised sodium carbonate, 2·5 grams sodium chloride, and 0·4 gram of basic bismuth nitrate are finely powdered and intimately mixed, placed in an earthen crucible, covered with a layer of coarsely powdered starch 2 cm. deep, and heated in a coke fire at bright redness for 5 hours, and allowed to cool during 10 or 12 hours.

As Verneuil has observed in the case of the calcium compound, strontium sulphide loses its power of phosphorescence if finely powdered, but regains it more or less completely if mixed with starch and heated at very bright redness for about 5 hours.

The researches of Verneuil and of the author show that the property of phosphorescence of sulphides of the calcium group is confined to sulphides of the type MS, and is dependent on the presence of small quantities of alkali compounds and of bismuth. Further experiments indicate that in the case of strontium sulphide the presence of a small quantity of sulphate is essential, but if the sulphide is oxidised to any considerable extent its phosphorescent properties disappear.

The strontium sulphide prepared as above contains a small quantity of sulphate, but offers considerable resistance to oxidation, probably owing to the fact that it consists of small rounded grains with a smooth fused surface. It is also but slowly affected by water and even

by dilute acids. It would seem that this structure has considerable influence on the phosphorescent power of the compound.

C. H. B.

**Basic Salts of Cadmium.** By TASSILLY (*Compt. rend.*, 1897, **124**, 1022—1024).—The salts $CdI_2,CdO,3H_2O$ and $CdBr_2,CdO,3H_2O$ are obtained by heating cadmium oxide in sealed tubes at 200° with a concentrated solution of cadmium iodide or bromide, as the case may be. They are distinctly crystallised, and the crystals act on polarised light. Water has very little action on them, and they are stable in pure dry air at 120°.

When ammonia is added to solutions of cadmium salts, the product is usually a mixture of a basic salt and an ammoniacal salt, but the formation of the latter can be avoided either by strictly limiting the quantity of ammonia, or by using very dilute solutions of both the ammonia and the cadmium salt. In the latter case, the basic salts obtained as precipitates, $CdBr_2,CdO,H_2O$ and $CdI_2,CdO,H_2O$, are of the same type as the oxychloride described by Habermann; the ammoniacal compounds can be crystallised from the mother liquid and are identical with those obtained by dissolving cadmium salts in ammonia, $CdX_2,2NH_3$. The yield of basic salt is highest with the chloride and lowest with the iodide, whereas the yield of ammoniacal compound follows the reverse order. The basic salts formed by precipitation are decomposed by water. C. H. B.

**Basic Nitrates.** By NICOLES ATHANASESCO (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1078—1081. Compare Abstr., 1895, ii, 315).—The basic lead nitrate, $N_2O_5,6PbO,H_2O$, previously described (*Bull. Soc. Chim.*, 1895, [iii], **14**, 175), is also obtained when lead nitrate is left in contact with an excess of aqueous ammonia for a year. When a concentrated solution of zinc nitrate (2 of solid to 1 of water) is heated in sealed tubes for several hours at 310°, the basic nitrate,

$$HNO_3,2ZnO,H_2O,$$

is formed; it crystallises in small, white needles decomposing above 200°, and is insoluble in water, but dissolves in dilute acids. Attempts to prepare the basic nitrate, $Zn(NO_3)_2,7ZnO,4H_2O$, by the incomplete precipitation of zinc nitrate solution with ammonia proved unsuccessful. When a 50 per cent. solution of zinc nitrate is boiled with metallic zinc for about a day, a basic nitrate, $N_2O_5,4ZnO + 4H_2O$, is formed, which crystallises in colourless needles, and loses its water at about 130°.

J. J. S.

**Mercury Haloid Double Compounds.** By THEODOR HARTH (*Zeit. anorg. Chem.*, 1897, **14**, 323—353).—The present research was undertaken to determine what salts are formed when the following mixtures are dissolved in water: (1) $HgCl_2,2KBr$, (2) $HgBr_2,2KCl$, (3) $HgCl_2,2KCN$, (4) $Hg(CN)_2,2KCl$, (5) $HgBr_2,2KCN$, (6) $Hg(CN)_2,2KBr$; and also how long the reaction takes before equilibrium is established. Solutions of the mercury salts were prepared of about 1 per cent. strength, and the potassium salt solution of such a strength that, on mixing the two solutions in equal volumes, the salts were in the proportions given above; 50 c.c. of the double salt solution

is then extracted with ether, whereby the mercury salt is dissolved and these are then analysed.

With mixtures of mercuric chloride and potassium bromide, and of mercuric bromide with potassium chloride, all the mercury is present as mercuric bromide, both when the solution is extracted 5 minutes after mixing and also after 24 hours. With mixtures of mercuric chloride and potassium cyanide and mercuric cyanide and potassium chloride, and also with the cyanides and bromides, all the mercury is present as mercuric cyanide. In mixtures of mercuric iodide and potassium chloride and mercuric iodide and potassium bromide, all the mercury is present as iodide. In mixtures of mercuric iodide and potassium cyanide, all the mercury is present as cyanide. Double decomposition takes place in all cases in which heat is evolved, and when the heat of formation of the salts, which would be formed by double decomposition, is less than that of the original salts, no double decomposition takes place.

From the above results, it is evident that the products formed by the mixtures $HgCl_2 + 2KBr$ and $HgBr_2 + 2KCl$ are identical; also the products formed by mixing $HgCl_2$ with $2KCN$ and $Hg(CN)_2$ with $2KCl$; as well as the products formed by mixing $HgBr_2$ with $2KCN$ and $Hg(CN)_2$ with $2KBr$.

Determinations of the electric conductivity of the double salts $HgCl_2Br_2K_2$ and $Hg(CN)_2Cl_2K_2$, show that the conductivity is only very slightly higher for the double salt than for potassium chloride, and this behaviour is not in accordance with the constitutional formula $Hg\begin{matrix}Cl_2\\Br_2\end{matrix}\Big\}K_2$ assigned to these compounds by Werner.

E. C. R.

**Purification of Cerium.** By GRÉGOIRE WYROUBOFF and AUGUSTE V. L. VERNEUIL (*Compt. rend.*, 1897, **124**, 1230—1233, and Henri Moissan, *ibid.*, 1233).—The difficulty of purifying cerium arises from its tendency to form an intermediate oxide, $Ce_3O_4,3CeO$, in which the mononoxide may be more or less completely replaced by lanthanum, didymium, and other oxides. In order to prevent the formation of this oxide, the oxides obtained by heating the oxalates are dissolved in nitric acid and the solution evaporated to a syrup, diluted until it contains only about 4 per cent. of the oxides, and ammonium nitrate added until the solution contains about 5 per cent. of it. The intermediate oxide is thus completely decomposed and the whole of the oxide, $Ce_3O_4$, is precipitated in the form of the basic salt, $(Ce_3O_4)_4N_2O_5$. The precipitate is washed with a 5 per cent. solution of ammonium nitrate and is quite free from didymium and lanthanum and the yttrium metals. The cerium in the solution may be recovered by precipitating it as oxalate and repeating the process.

When the oxides contain more than 50 per cent. of cerium, they are not entirely soluble in nitric acid, and in this case the oxalates are dissolved in nitric acid and mixed with hydrogen peroxide and ammonia and boiled, the cerosoceric oxide thus formed being washed and afterwards dissolved in nitric acid.

Any thorium in the cerium oxide is precipitated with the oxide $Ce_3O_4$,

and consequently the cerium recovered from the mother liquor is free from thorium as well as from the other impurities. In any case, however, it is easy to remove thorium by treating the oxalates, or, better, the nitrates, in neutral solution, with a concentrated solution of ammonium carbonate mixed with ammonia, the last traces being separated by fractional crystallisation of the sulphates, the thorium remaining in the mother liquor. Iron is removed by repeated precipitation with oxalic acid in hot acid solutions; or by heating the sulphate at 400—450°, when the iron becomes insoluble. Cerium thus purified has constant properties and a constant atomic weight.

According to Moissan, pure cerium can be obtained by preparing the carbide from cerium compounds which show no absorption spectrum, and then fractionally decomposing the carbide with dilute nitric acid. All the iron goes into the first solution; all the thorium remains in that portion of the carbide which is last attacked. C. H. B.

**Compounds of Phosphorus with Iron, Nickel, and Cobalt.** By A. GRANGER (*Bull. Soc. Chim.*, 1896, [iii], 15, 1086—1089).—Ferric chloride and phosphorus, when separately placed in two small boats and gently heated in a stream of carbonic anhydride, yield ferric phosphide and phosphorus pentachloride. *Ferric phosphide*, $Fe_2P_3$, which is deposited as small, brilliant, grey needles, is not magnetic and is not attacked by nitric or hydrochloric acid or by aqua regia, but dissolves slowly in potassium hypobromite solution. When raised to a dull red heat, it undergoes no change, but in the blowpipe flame it gives up phosphorus. Nickel and cobalt phosphides may be obtained in a similar manner. *Nickel phosphide* is grey and has a graphitic lustre, it also possesses a strongly marked schistose structure and is very friable. *Cobalt phosphide* is black and can easily be powdered. Both these compounds are less readily acted on by chlorine than is iron phosphide. The *phosphide*, $Fe_4P_3$, obtained when phosphorus trichloride acts on iron at a moderate heat, crystallises in small, grey prisms; the same compound is obtained when phosphate of iron is reduced with hydrogen or when metallic iron is heated with phosphorus iodide. The phosphides, $Co_2P$ and $Ni_2P$, obtained by the action of phosphorus trichloride on cobalt and nickel respectively, are also described. J. J. S.

**Constitution of Cobalt, Chromium and Rhodium Bases.** By SOFUS M. JÖRGENSEN (*Zeit. anorg. Chem.*, 1897, 14, 404—422).—*Praseo-* and *Violeo-cobalt Salts.*—In a previous paper (Abstr., 1895, ii, 47), the author has shown that the luteo-salts have a symmetrical constitution, as they are the most stable of the cobalt-ammonia-salts. And since the pentamineroseo-salts and the tetramineroseo-salts show a complete analogy with the preceding, they also probably have a symmetrical constitution. The isomeric flavo- and croceo-salts, $(NO_2)_2CoA_4X$, are dinitrotetramine salts of the praseo- and violeo-series; and the flavo-salts, on account of their near relation to the tetramineroseo-salts, have probably a symmetrical constitution. The praseo-salts, which are so easily obtained from the tetramine-salts, have probably also a symmetrical constitution. Hence it is

probable that the flavo-salts belong to the praseo-series, and the croceo-salts to the violeo-series. The relation between the flavo- and croceo-salts is very different; the former, when treated with hot concentrated hydrochloric acid, loses both its nitro-groups, whereas the latter loses only one. On the other hand, Werner (*Zeit. anorg. Chem.*, 8, 182) has found that praseo-salts, when warmed with sodium nitrite and acetic acid, are converted into croceo-salts. According to Werner's researches, the praseo-tetramine-purpureo-salts are violet; and this is the case with the only known series of these compounds, the chloro-aquotetramine salts. The praseo-chloride, when warmed with dilute hydrochloric acid, is converted into the chloro-aquotetramine chloride, and the green solution of acid dichloropraseo-sulphate soon changes to violet and deposits the chloro-aquotetramine sulphate. Hence the chloro-aquotetramine salts belong to the praseo-series. On the other hand, chloro-aquotetramine chloride is easily prepared by heating carbonato-tetramine chloride with dilute hydrochloric acid, and this reaction takes place in the cold with concentrated acid, whence it follows that the chloro-aquotetramine salts belong to the violeo-series. The formation of flavo-salts from carbonatotetramine-salts and of croceo-salts from praseo-chloride show that they belong to the violeo- and praseo-series respectively. On the other hand, flavo-salts are easily obtained from chloro-aquotetramine chloride, whence it follows that either the chloro-aquotetramine salts belong to the violeo-series, or that the flavo-salts belong to the praseo-series.

The flavo-salts belong, according to Werner, to the violeo-series. However, the flavo-chloride, when allowed to remain in the cold with concentrated hydrochloric acid, is completely converted into chloro-aquotetramine chloride, together with a very small quantity of praseo-chloride. When flavo-nitrate is boiled with dilute hydrochloric acid, it is converted into praseo- and aquo-tetramine salts. Hence the flavo-salts belong to the praseo-series. It is remarkable that the flavo-salts are so easily converted into compounds of the praseo-series, whereas the croceo-salts, which, according to Werner, belong to this series, do not yield chloro-aquotetramine chloride or praseo-chloride when treated with hydrochloric acid.

The diaquotetramine chloride, when warmed at 100° or with hydrochloric acid, is converted into chloro-aquotetramine chloride; the latter yields a red solution with dilute sodium hydroxide, which contains basic diaquotetramine chloride, and when treated with concentrated hydrochloric acid, yields tetramineroseo-chloride. Hence the chloro-aquotetramine salts and the diaquotetramine salts (tetramineroseo-salts) belong to the same series.

The praseo-chloride, when warmed with ammonium carbonate, is converted quantitatively into the carbonatotetramine chloride. Hence the typical violeo-salt belongs to the praseo-series, or the typical praseo-salt to the violeo-series.

The above results show that those differences between the praseo- and violeo-salts which are found in the cobalt ethylenediamine salts are not found in the cobalt-ammonia salts.

The ammonia group can only be arranged in one way as a bivalent radicle, whereas the ethylenediamine group can be arranged in two

$$\begin{array}{ccc} & \overset{C_2H_4}{\overbrace{\phantom{xxxxxxxx}}} & & \overset{C_2H_4}{\overbrace{\phantom{xxxxxxxxxxxx}}} \\ \text{ways, that is, } & -NH_2{\cdot}NH_2{\cdot}NH_2{\cdot}NH_2- & \text{ and } & -NH_2 \cdot NH_2{\cdot}NH_2{\cdot}NH_2- \\ & \underset{C_2H_4}{\underbrace{\phantom{xxxxxxxx}}} & & \underset{C_2H_4}{\underbrace{\phantom{xxxxxxxx}}} \end{array}$$

hence it is not necessary, in order to explain this isomerism, to assume that the cobalt atom has different valencies.

*Praseo- and Dichro-salts.*—The praseo-cobalt sulphate is easily prepared by treating the chloro-aquotetramine chloride (10 grams) with concentrated sulphuric acid (50 c.c.), and allowing the mixture to remain until a violet solution is obtained. The solution is then cooled with ice, and concentrated hydrochloric acid (50 c.c.) gradually added. After 24—28 hours, the green praseo-cobalt salt which crystallises out is washed free from hydrochloric acid with dilute sulphuric acid, and then with absolute alcohol. The yield is very nearly theoretical. If the praseo-salt is washed twice with dilute sulphuric acid in order to extract traces of pentamine salts, and then washed with dilute hydrochloric acid until free from sulphuric acid, a theoretical yield of praseo-cobalt chloride is obtained. Praseo-salts are also obtained pure and in theoretical quantities from diaquotetraminecobalt sulphate, which is easily obtained from carbonatotetraminecobalt sulphate. The diaquotetramine sulphate (10 grams) is dissolved in concentrated sulphuric acid (50 c.c.), allowed to remain 24 hours, then mixed with concentrated hydrochloric acid (50 c.c.), and allowed to remain 48 hours, when the praseo-salt which crystallises out is either washed free from hydrochloric acid by dilute sulphuric acid, or free from sulphuric acid by hydrochloric acid, and the praseo-sulphate or chloride then washed with absolute alcohol. Praseo-cobalt chloride crystallises with $1H_2O$ and is not anhydrous as stated by Klein (*Zeit. anorg. Chem.*, **14**, 28). The bromide, is obtained from the acid sulphate in a similar manner to the chloride. The chlorobromide becomes bright blue if kept at 100° for some 6 weeks; it then loses 25 per cent. in weight, corresponding with a loss of $2NH_3 + Cl$.

The conversion of chloride into sulphate, and of the sulphate into chloride, which takes place so easily in the praseo-salts, also takes place in the dichro-salts. The dichro-chloride, in an analogous manner to the praseo-chloride, yields a dichlorosulphate from which a dichloronitrate can be obtained. The dichro-chloride is obtained by heating the triamine nitrite with concentrated hydrochloric acid.

*Acid dichloroaquotriamine cobalt sulphate*, $Cl_2Co(NH_3)_3OH_2{\cdot}SO_4H$, is obtained by treating the dichro-chloride with 50 per cent. sulphuric acid, and after the mixture has remained 24 hours, washing the product free from hydrochloric acid with dilute sulphuric acid; it crystallises in microscopic, greyish-green needles. When treated with hydrochloric acid, it is converted into the dichro-chloride. It dissolves in 5—6 parts of cold water to a greenish solution, which, however, soon changes to violet, and when mixed with hydrochloric acid, yields dichro-cobalt chloride and not the chlorodiaquotriamine chloride. The *silver salt*, $Cl_2Co(NH_3)_3OH_2{\cdot}SO_4Ag$, is obtained as a bright, olive-green precipitate by treating the compound with silver nitrate. It is easily decomposed by cold water into silver chloride and a blue solution.

*Dichloroaquotriamine cobalt nitrate*, $Cl_2Co(NH_3)_3OH_2 \cdot NO_3$, is obtained by treating the preceding salt with dilute nitric acid. It crystallises in very small, dichromatic prisms.

*Chlorodiaquotriamine cobalt sulphate*, $ClOH_2Co(NH_3)_3OH_2 : SO_4$, is formed when a cold aqueous solution of the dichro-sulphate is kept. It crystallises in violet-red crusts of rhombic tablets, which are sparingly soluble in cold water, and insoluble in dilute alcohol. When allowed to remain for 24 hours with dilute hydrochloric acid, it is converted into the dichro-chloride. A dilute solution of the dichro-sulphate, after some time, deposits yellow prisms which are probably the triaquotriamine chloride sulphate. E. C. R.

**Colloidal Tungstic Acid.** By ALEXANDER P. SABANÉEFF (*Zeit. anorg. Chem.*, 1897, **14**, 354—360).—The author has prepared the substance described by Graham (*Proc. Roy. Soc.*, 1864, **13**, 340) as colloidal tungstic acid, and finds that it is an amorphous form of sodium metatungstate. It has the properties ascribed to it by Graham except that the colour of the solution is generally blue, not green; when boiled with dilute acids, it does not give a precipitate, with concentrated acids, however, it yields a yellow precipitate of tungstic hydroxide. The yield amounts to about 20—23 per cent. of the sodium tungstate employed. The author was unable to obtain a product free from alkali either by adding hydrochloric acid during the dialysis or by the action of hydrochloric acid on the colloidal salt. In order to obtain the colloidal salt, it is necessary to employ the sodium tungstate and hydrochloric acid in the proportion $2Na_2WO_4 : 3HCl$, but the reaction proceeds only partially according to the equation $4Na_2WO_4 + 6HCl = Na_2O,4WO_3 + 6NaCl$. A solution of sodium metatungstate and sodium chloride does not behave in the same manner as a solution of the same concentration of sodium tungstate and hydrochloric acid. The latter gives with the excess of acid a precipitate of tungstic hydroxide, whereas the former remains unaltered even on boiling. When the mixture of $4Na_2WO_4$ and $6HCl$ is evaporated on the water bath or at 40°, crystalline sodium paratungstate first separates, then sodium chloride and a double salt of the composition $Na_2O,4WO_3,2NaCl,H_2O$; the mother liquor contains sodium metatungstate, together with a small quantity of sodium chloride.

The crystalline and colloidal modifications of sodium metatungstate have very similar properties. The solutions are neither decomposed nor precipitated by ordinary hydrochloric acid, but the addition of fuming acid causes a precipitation; with alkali, either the para- or the normal salt is formed, according to the proportion added. Both modifications lose the same percentage of water when heated at 100° and 200°, and when heated to redness become insoluble in water. They show an equal molecular conductivity in dilute solutions, but in stronger solutions the molecular conductivity of the colloidal modification is somewhat less. E. C. R.

**Thorium.** By GERHARD KRÜSS (*Zeit. anorg. Chem.*, 1897, **14**, 361—366).—Thorium hydroxide is most easily prepared by treating solid thorium sulphate with ammonia, taking care to stir the mixture well in order to complete the reaction. The product, which is

a heavy powder easily washed, is boiled with ammonia in order to extract the last traces of sulphate, and then washed with water.

*Thorium chloride*, $ThCl_4 + 7H_2O$, is obtained by treating thorium hydroxide suspended in absolute alcohol with hydrogen chloride, and allowing the solution thus obtained to crystallise in a vacuum over sodium hydroxide and sulphuric acid. It crystallises in rhombic pyramids, deliquesces in the air, and effloresces when allowed to remain in a desiccator, water and hydrogen chloride being given off. The anhydrous chloride cannot be prepared by heating the crystals in a current of hydrogen chloride or chlorine, as under these conditions a mixture containing oxychloride is obtained. When heated, it decomposes with formation of thorium oxide and evolution of water and hydrogen chloride. It is very easily soluble in water and alcohol, yielding an acid solution, and the addition of ether to the alcoholic solution causes a precipitate of the unaltered salt. When crystallised from alcohol containing water, it separates in slender needles with 11 to 12 $H_2O$, as described by Cleve.

*Thorium Oxychloride.*—The preparation of a pure compound of the composition $ThOCl_2$, has not been accomplished; nothing but impure products were obtained by heating the chloride in a current of hydrogen chloride or chlorine, or by heating the hydroxide in a current of hydrogen chloride. The product obtained by heating the crystalline chloride alone always contains more thorium oxide than is required by the above formula. E. C. R.

**Constitution of Platosemiamine Compounds.** By ALFONSO COSSA (*Zeit. anorg. Chem.*, 1897, 14, 366—373).—Mainly a criticism of Werner's views on the constitution of the ammonio-platinum compounds.

## Mineralogical Chemistry.

**Composition and Specific Gravity of Sulfoborite.** By KONSTANTIN THADDÉEFF (*Zeits. Kryst. Min.*, 1897, 28, 264—275).—In the previous analysis of sulfoborite by Naupert and Wense (Abstr., 1893, ii, 325; 1895, ii, 276), the determinations of boric acid and water are unsatisfactory. A new examination gives as the mean of five partial analyses:

| MgO. | $SO_3$. | $B_2O_3$ | $Fe_2O_3$. | Loss on ignition. | Loss at 110—170°. | Insol. | Total. |
|---|---|---|---|---|---|---|---|
| 33·48 | 22·46 | 19·79 | 0·11 | 23·43 | 0·10 | 0·32 | 99·69 |

Direct determinations of the water by fusing with sodium and potassium carbonates (Sipöcz's method) gave 20·01 and 19·47 per cent., but as caustic soda may have been formed, these are probably too low. These analyses give the molecular ratios $MgO : SO_3 : B_2O_3 : H_2O = 2·98 : 1 : 1·01 : 4·66$, and the new formula, $MgSO_4,Mg_2B_2O_5,4\frac{1}{2}H_2O = 4MgHBO_3,2MgSO_4,7H_2O$. The molecular ratio of the water is still

unsatisfactory, this being due to the partial decomposition of the material analysed.

As the crystals are acted on by water, the specific gravity determinations were made by weighing the mixture of methylene iodide and benzene in which the crystals floated, or by weighing the crystals with benzene in a pyknometer. Clear fresh crystals gave sp. gr. = 2·440. Unselected crystals gave 2·28—2·445, and the material analysed gave 2·415. L. J. S.

**Gersbyite and Munkrudite.** By LARS J. IGELSTRÖM (*Zeits. Kryst. Min.*, 1897, **28**, 310—312).—These two "new minerals" occur with "munkforsite" (this vol., ii, 267) in the damourite quartzite at Dicksberg, Sweden. Gersbyite is a blue mineral closely resembling lazulite in appearance; from five analyses, which vary considerably, the formula is given as $3(Fe,Mn,Ca,Mg)O,P_2O_5 + 3(3Al_2O_3,P_2O_5) + 17H_2O$; this is more basic than lazulite.

Munkrudite is a white, transparent, crystallised mineral, which occurs mixed with pyrites; it contains phosphoric acid (about 12 per cent.), sulphuric acid, ferrous oxide, and lime; it is therefore related to svanbergite and "munkforsite," but in outward appearance it is very different from the latter. L. J. S.

**[Augite from Montana.]** By LOUIS V. PIRSSON (*Zeits. Kryst. Min.*, 1897, **28**, 333; from *Bull. Geol. Soc. Amer.*, 1895, **6**, 389—422. Compare Abstr., 1896, ii, 192).—In a paper by W. H. Weed and L. V. Pirsson on the igneous rocks of the Highwood Mountains of Montana, a description is given of the augite which forms about half of the new rock shonkinite from Square Butte. It occurs as easily isolated, greenish-black crystals over 1 cm. in length, and of the usual habit. Analysis gave:

| $SiO_2$. | $TiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MnO. | MgO. | CaO. | $Na_2O$. | $K_2O$. | $H_2O$ (at 100°). | Total. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 49·42 | 0·55 | 4·28 | 2·86 | 5·56 | 0·10 | 13·58 | 22·35 | 1·04 | 0·38 | 0·09 | 100·21 |

This gives the formula $13Ca(Mg,Fe)Si_2O_6 + 2(Na_2,R'')(Al,Fe)_2SiO_6$.
L. J. S.

**Garnet from the Turjinsk mines.** By E. VON FEDOROW (*Zeits. Kryst. Min.*, 1896, **28**, 276—290).—The important ore deposits, consisting mainly of copper pyrites, of the Bogoslowsk district in the Urals, occur near the margins of an eruptive mass of augite-garnet rock. The garnets are of two kinds: a dark brown (anal. I), and a pale green which in thin sections is colourless (anal. II). The difference in colour of these garnets is not explained by the chemical composition.

| | $SiO_2$. | $Fe_2O_3$. | FeO. | CaO. | $Al_2O_3$. | $Mn_2O_3$. |
|---|---|---|---|---|---|---|
| I. | 34·98 | 23·77 | 3·33 | 34·06 | 3·32 | 1·22 |
| II. | 38·22 | 25·62 | 1·96 | 31·80 | 2·11 | 0·58 |

The main portion of the paper is occupied by a description of the optical anomalies of the light coloured garnet; the dark coloured is isotropic. L. J. S.

**Analysis of a Meteoric Stone which fell at Madrid, February 10th, 1896.** By SANTIAGO BONILLA MIRAT (*Bull. Soc. Chim.*, 1897, [iii],

15, 1070).—The analysis of this meteoric stone gave the following results :

| $SiO_2$ | MgO. | Fe. | FeS. | $Fe_2O_3$. | $Al_2O_3$. | Ni. | CaO. | $MnO_2$. |
|---|---|---|---|---|---|---|---|---|
| 58·86 | 15·95 | 7·75 | 7·23 | 5·11 | 2·36 | 1·30 | 0·51 | 0·08 |

Phosphorus, chromium, copper, sodium, potassium, lithium, and nitrogenous compounds, which amounted in all to 0·85 per cent., bring the total to 100.

The sp. gr. = 3·6189 at 15° ; hygroscopic moisture amounted to 0·2841 per cent. M. O. F.

## Chemistry of Vegetable Physiology and Agriculture.

**Fatty Matter of Beer Yeast.** By ERNEST GÉRARD and P. DAREXY (*J. Pharm.*, 1897, [vi], 5, 275—280).—The authors find that the fatty matter obtained from yeast contains stearic and palmitic acids together with a small quantity of butyric acid. The acids occur to a certain extent as their glyceryl salts, and also probably in the free form. J. J. S.

**Formation of "Fruit Ethers" by Yeasts in Green Malt and in Worts.** By PAUL LINDNER (*Bied. Centr.*, 1897, 26, 339—340 ; from *Wochensch. f. Brauerei*, 1896, No. 23, 552).—The intense odour of "fruit-ether" (ethereal salts) observed when green malt is kept, with abundant aëration, is due to a yeast nearly related to *Saccharomyces anomalus.* If the malt is too wet, the yeast production is less, and an odour of sour beet-root is produced. The formation of ethereal salts (probably ethylic acetoacetate) prevents the development of bacteria ; and the striking stability of many surface-yeasts is no doubt connected with the sour ethereal odour which they nearly always possess.

In the case of various fruits, such as strawberries, the ethereal salts act as preservatives from putrefaction. *Saccharomyces apiculatus*, and other dextrose yeasts, also give rise to production of ethereal salts, especially under conditions of aëration. Wine loses, perhaps, some of its bouquet when so much pure yeast is added to the must that the *S. apiculatus* is unable to produce ethereal salts. N. H. J. M.

**Fixation of Free Nitrogen by the Bacillus of Leguminous Nodules.** By MAZÉ (*Ann. Inst. Pasteur*, 1897, 44—54).—The very slight gain of nitrogen hitherto observed in cultivations of the leguminous nodule bacillus is attributed to the fact that nitrogen has only been supplied in the uncombined state, or as ammonia and asparagine, whilst under natural conditions the bacillus has, from the commencement, a store of proteid nitrogen. The amount of hydrocarbon furnished (as in the experiments of Frank, Laurent and Beyerinck) has also been too limited. Moreover, the branched, forked, and flattened forms of the nodules indicate that a sufficient supply of oxygen is of importance.

By cultivating the bacillus on the surface of solid media containing

infusion of haricots, saccharose, sodium chloride, and sodium hydrogen carbonate, very abundant growth was rapidly obtained. The experiments were made in a series of flasks through which air free from combined nitrogen was passed (20 litres per day). The first experiment, which lasted 14 days, showed a gain (in three flasks) of 40·8 milligrams of nitrogen, the initial and final amounts of nitrogen being respectively 62·1 and 102·9 milligrams. Supposing the whole of the sugar present to have been consumed, the relation of nitrogen gained to sugar consumed would be $0·0408 \div 3·075 = 0·013$. Similar results were obtained in a second experiment: nitrogen at commencement = 70·7 milligrams; at conclusion 118·2 milligrams; gain = 47·5 milligrams.

A third experiment was made, employing a liquid instead of a solid medium. The cultures were made in two flasks, each containing 50 c.c. of haricot-broth with sugar (2·6 per cent.), sodium chloride (0·1 per cent.), and a trace of hydrogen sodium carbonate. The experiment lasted 16 days, by which time the whole of the sugar was consumed. The nitrogen fixed amounted to $45·8 - 22·4 = 23·4$ milligrams, and the relation of nitrogen gained to sugar consumed was $0·0234 \div 2·6$.

The results show, therefore, that the bacillus, when cultivated under suitable conditions, readily develops, at the same time exercising its important function of assimilating elementary nitrogen. Symbiosis is not necessary to explain nitrogen fixation, which is effected by the bacillus alone (compare Duclaux, *Ann. Inst. Pasteur*, 1894, 728). The leguminous plant furnishes the bacillus with hydrocarbons and organic nitrogen, thus supplying the organism with the energy necessary to enable it to fix nitrogen.

With regard to the relation of nitrogen fixed to sugar consumed, it is pointed out that the percentages of nitrogen and sugar in sugar-beet are about 0·224 and 14·0. The relation $0·224 \div 14·0 = 0·016$ is rather higher than the relation shown by experiment 3. It is, however, clear that sugar-beet, in its second year, could easily obtain its nitrogen from the air if its accumulated energy could be so utilised. The relation of leaf surface to total weight is at least as great in clover and lucerne as in beet-root, whilst the vegetative period of *Leguminosæ* is longer than that of beet-root. The minimum temperature at which vegetation is manifested is also in favour of the *Leguminosæ*.

N. H. J. M.

**Function of Tannin in Plants and especially in Fruits.** By C. Gerber (*Compt. rend.*, 1897, **124**, 1106—1109).—In the respiration of soft fruits containing tannin, the volume of the carbonic anhydride evolved is less than that of the oxygen absorbed so long as any tannin remains unaltered. As soon as all the tannin has disappeared, pectin is produced. If the temperature is so low that the cellular activity is not great, the respiration quotient remains lower than unity, but if the temperature is so high that the cellular activity requires more energy than is furnished by the free oxygen, the cellules obtain the necessary energy from the alcoholic fermentation of the sugars, the carbonic anhydride produced by it being added to that produced by respiration, and thus giving a quotient higher than unity. It follows that one of the principal functions of tannins in fruits is to prevent pectic transformations, and thus check the fermentation of the sugars.

Direct experiments with the fruit of *Dyospyros kaki* show that the disappearance of tannins does not involve an increase in the amount of sugar, and experiments on the respiration of *Sterigmatocystis nigra* on a solution of nut-gall tannin lead to the same conclusion. In fruits containing tannins, the latter disappear as the result of complete oxidation, without forming any carbohydrates. C. H. B.

**Analysis and Composition of Stick Liquorice.** By G. Py (*J. Pharm*, 1897, [vi], **5**, 280—284).—The author has analysed numerous samples of "Spanish liquorice." In each case, the moisture, ash, alcoholic extract, organic substances insoluble in alcohol of 75°, ammonium glycyrrhizate, total nitrogen, and glucose were estimated. Directions are also given for testing for gelatin and gum. J. J. S.

**The Carbohydrates of Wheat, Maize, Flour, and Bread.** By Winthrop E. Stone (*Office of Expt. Stat. U.S. Agric. Dept. Bul.*, **34**, 1896, 7—28).—The carbohydrates present in grains and in flour were determined, and the changes which take place during the process of bread-making investigated. The analytical methods, which are described, included the separation and estimation of sucrose, invert-sugar, dextrin, starch, pentosans and hemicelluloses, and crude fibre. The process of making the bread is fully described. The following numbers show the percentage amounts of carbohydrates in the dry matter of wheat, maize, flour, and bread:—

| | | Sucrose. | Invert. sugar. | Dextrin. | Soluble starch. | Normal starch. | Pentosans. | Crude fibre. |
|---|---|---|---|---|---|---|---|---|
| Winter wheat | grain... | 0·51 | 0·08 | 0·27 | 0·00 | 30·94 | 4·54 | 2·68 |
| | bread... | 0·014 | 0·10 | 0·68 | 1·37 | 27·93 | 4·16 | 2·70 |
| Spring wheat | grain... | 0·72 | 0·00 | 0·41 | 0·00 | 30·36 | 4·37 | 2·51 |
| | bread... | 0·05 | 0·32 | 0·23 | 2·36 | 27·08 | 4·34 | 2·42 |
| Winter wheat | flour ... | 0·20 | 0·00 | 1·06 | 0·00 | 34·04 | 0·00 | 0·25 |
| | bread... | 0·15 | 0·38 | 0·91 | 1·74 | 31·99 | 0·00 | 0·17 |
| Spring wheat | flour ... | 0·18 | 0·00 | 0·90 | 0·00 | 46·19 | 0·00 | 0·25 |
| | bread... | 0·06 | 0·37 | 0·27 | 1·99 | 39·71 | 0·00 | 0·34 |
| Maize | grain... | 0·27 | 0·00 | 0·32 | 0·00 | 42·50 | 5·14 | 1·99 |
| | bread... | 0·16 | 0·19 | 0·00 | 2·80 | 40·37 | 3·54 | 2·22 |

Flour made from wheat contains less sucrose and crude fibre than the grain; invert-sugar and pentosans disappear entirely. In making bread, there is a loss of carbohydrates amounting to 1—5 per cent. of the total dry matter; there is a diminution in the amount of sugar, and a tendency to convert the starch into soluble and fermentable forms. This change of starch, however, is confined to the more exposed portions of loaves; in the author's experiments, the amount of starch changed did not average more than 10 per cent. of the total starch.

The temperature of the interior of the loaves baked in the usual manner never exceeded 99°. The loss of weight in "raising" and baking bread amounts to 12—20 per cent., but the actual loss of dry substance is only 3—4 per cent.

All the carbohydrates originally present in flour were found in the bread, and the bread contained, besides, more or less "soluble starch." N. H. J. M.

**Action of Enzymic Ferments on Starches of Different Origin.** By Winthrop E. Stone (*Office of Expt. Stat. U.S. Agric. Dept.*

*Bul.*, **34**, 1896, 29—44).—The starches selected for experiment were (1) maize, (2) wheat, (3) rice, (4) potato, and (5) sweet potato (*Batatas edulis*). The enzymes were diastase (from freshly-prepared malt), ptyalin (from human saliva), commercial pancreatin, pancreatin prepared from the pancreas of freshly-killed swine, and "Taka-diastase," the enzyme developed by the fungus *Eurotium oryzæ*.

The results of the experiments show that the different starches vary considerably in their susceptibility to the action of the ferments, some requiring eighty times as long as others for complete solution or saccharification.

Beginning with the starch most readily changed, the relative order is: for malt extract—sweet potato, potato, wheat, and maize; for saliva—potato, sweet potato, maize, rice, and wheat; for pancreatic fluids—potato, sweet potato, and maize, with wheat and rice unchanged; with "Taka-diastase," potato-starch was the most quickly changed. In some cases, the rapidity of the change is proportional to the concentration of the ferment solution. It is assumed that, in the processes of digestion, the starches would have the same relative susceptibility as they showed in the above experiments. N. H. J. M.

**Origin of Silica in Incrustations and Deposits of the Beet-root Sugar Manufacture: Solubility of Calcium Silicate in Saccharine Solutions.** By J. Weisberg (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1097—1100).—The author considers that the greater amount of silica and calcium silicate found in deposits and incrustations of beet-root juice is derived from the lime used in the purification of the juice. The lime obtains its silica, not only from the limestone used, but also from the coke and brickwork of the limekilns. It has been proved that saccharine solutions dissolve calcium silicate more readily than pure water does, and also that the amount of salt dissolved increases with the strength of the saccharine solution. Hot solutions dissolve more calcium silicate than cold, and the presence of carbonic anhydride increases the solubility of lime, and also of calcium silicate in saccharine solutions. In the latter case, part of the calcium silicate is decomposed, yielding calcium carbonate and free silica. It has been found that calcined silica is much less soluble in saccharine solutions than the partially dried compound. J. J. S.

**Analyses of Spurrey.** By B. Böggild (*Bied. Centr.*, 1897, **26**, 347; from *Ugeskrift f. Landmœnd*, 1897).—In certain parts of Denmark, the seeds of uncultivated spurrey are collected, ground, and fed, whilst in other parts the plant is cultivated (especially on peaty soils) for the production of hay and seeds. The yield of spurrey hay is about 2000 kilos. per hectare (about 16 cwt. per acre). The following analyses show that the hay is nutritious as compared with average Danish hay, and that the seeds are not so excessively oily as was sometimes supposed:—

| | Water. | Crude protein. | Crude fat. | Crude fibre. | N. free extract. | Ash. |
|---|---|---|---|---|---|---|
| Ordinary hay ......... | 18·59 | 7·50 | 1·54 | 27·89 | 38·13 | 6·35 |
| Spurrey hay ......... | 13·71 | 9·19 | 2·86 | 23·75 | 44·68 | 5·81 |
| Seeds of *Spergula arvensis vulgaris* | 9·85 | 11·43 | 8·92 | 13·87 | 36·63 | 19·30 |
| Seeds of *S. Maxima* | 12·15 | 13·06 | 9·56 | 8·63 | 53·60 | 3·00 |

N. H. J. M.

**Soils of Cameroon, Senegambia, and German East Africa: Improved Method of Soil Analysis.** By FERDINAND WOHLTMANN and H. KRATZ (*Bied. Centr.*, 1897, **26**, 292—296; from *J. Landw.*, 1896, 211).—The mineral food-constituents present in soil are extracted by macerating the soil (450 grams) for 48 hours with cold hydrochloric acid (sp. gr. = 1·15; 1500 c.c.). In the case of soil containing much iron and alumina (25—30 per cent.), twice as much hydrochloric acid is employed. The single constituents are estimated, as a rule, by the ordinary methods. Silica is estimated as usual by evaporating down, &c., but in soils containing much iron and alumina, about 10 grams of sodium chloride is added to the solution to prevent the production of insoluble compounds. Lemmermann points out that the addition of sodium chloride is unnecessary, as the insolubility produced in presence of iron and alumina refers only to water; moderate heating after moistening with strong hydrochloric acid will always render the compounds soluble. N. H. J. M.

**The Function of Humic Substances in the Fertility of Soils.** By ARMAND GAUTIER (*Compt. rend.*, 1897, **124**, 1205—1206).—According to the author's view, the chief function of the humic substances in the soil is to afford nutriment for the algæ and microbes which have the power of fixing atmospheric nitrogen. In the absence of such nutriment, the algæ and microbes are more or less starved, and their activity in fixing nitrogen is thereby greatly reduced, with the result that the soil remains comparatively unfertile. C. H. B.

---

## Analytical Chemistry.

**Apparatus for the Industrial Analysis of Gases.** By LÉO VIGNON (*Compt. rend.*, 1897, **124**, 1244—1246).—This apparatus consists of a horizontal tube closed at one end by a stopcock, whilst the other end terminates in a vertical explosion vessel, fitted at its upper end with a stopcock, and at its lower with a movable mercury reservoir. Between the extremities of the horizontal tube there are attached to it by means of vertical side tubes fitted with stopcocks (1) a vertical measuring tube, which is at the end of the horizontal tube furthest away from the explosion tube. This tube is attached at its lower end to a movable mercury reservoir, and is surrounded by a water jacket. (2) One, two, or more cylindrical bulbs containing the necessary absorption reagents. These pipettes have vertical stems below the bulbs as well as above, and their lower ends dip into the reagents contained in Woulff's bottles. The gas is passed from one tube or bulb to another by means of the movable mercury reservoir. C. H. B.

**Separation of Tellurium from Antimony.** By WILHELM MUTHMANN and E. SCHRÖDER (*Zeit. anorg. Chem.*, 1897, **14**, 432—436). —The method is based on the decomposition of tellurium sulphide and

the insolubility of the resulting tellurium in somewhat concentrated hydrochloric acid.

The solution of the two metals in hydrochloric acid is mixed with tartaric acid, and completely precipitated with hydrogen sulphide; the precipitate is separated and washed, and digested with a warm solution of potassium sulphide, whereby all the tellurium is dissolved. This solution, which should not contain a large excess of potassium sulphide, is gradually added to a solution containing 20 per cent. hydrogen chloride and some tartaric acid, and digested until the precipitate becomes flocculent. The precipitate, which consists of a mixture of tellurium and sulphur, is separated and washed with hot hydrochloric acid, and then with water containing tartaric acid until quite free from antimony. The antimony is then determined in the filtrate by any of the ordinary methods. The precipitate of tellurium and sulphur is dissolved in fuming nitric acid, and the tellurium weighed either as metal or dioxide. The results are accurate.

An analysis of "Blättererze," from Nagyág, by this method gave the following results: Pb, 53·55; Au, 9·47; Sb, 6·05; Te, 18·99; S, 11·895; quartz, 0·56 per cent., which corresponds to the empirical formula $Pb_{10}Au_2Sb_2Te_6S_{15}$. E. C. R.

**Extremely Sensitive Reagent for Detection and Colorimetric Estimation of Nitrous Acid.** By E. RIEGLER (*Zeit. anal. Chem.*, 1897, **36**, 377—378).—The author has prepared a reagent which is twenty times as sensitive as the 1 : 4-naphthylaminesulphonic acid previously recommended (this vol., ii, 230). A solution is made of 2 grams of chemically pure sodium 1 : 4-naphthylaminesulphonate and 1 gram of β-naphthol (puriss.) in 200 c.c. and filtered. The solution is colourless, but has a violet-blue fluorescence. It may be preserved unchanged in the dark. It is even better to mix the dry substances intimately in a mortar and preserve the dry mixture, adding a few centigrams of it to the liquid to be tested. Both for qualitative and quantitative tests, the operations are the same as with naphthylaminesulphonic acid (pp. 230, 385), except that the type solution of nitrite should be $\frac{1}{10}$th the strength there recommended, since this reagent is capable of detecting 1 part and estimating 5 parts of $N_2O_3$ in 100 millions of water. M. J. S.

**Combustion Boat with Partitions.** By ERNST MURMANN (*Zeit. anal. Chem.*, 1897, **36**, 380, 381).—Substances which fuse when heated are liable to flow to the cooler end of the ordinary boat, and, when reached by the heat, to decompose too rapidly for accurate work. By dividing the boat into compartments, this difficulty is entirely obviated. M. J. S.

**Precipitation of Zinc as Sulphide.** By JEAN MEUNIER (*Compt. rend.*, 1897, **124**, 1151—1152).—The difficulty usually experienced in obtaining zinc sulphide in a form that is readily filtered and washed arises from the use of an excess of the precipitant. The solution should be carefully mixed with ammonia until the precipitate is just redissolved. A slow current of hydrogen sulphide is passed into the liquid, but is discontinued as soon as precipitation is complete, this

point being ascertained by testing a few drops of the liquid on a white plate with a drop of ferrous sulphate solution. The precipitate settles rapidly, and is readily filtered and washed, the operations being more rapid if the liquid is warm. The precipitation is not interfered with by relatively large quantities of ammonium salts.

C. H. B.

**Employment of Ammonium Carbonate in Water Analysis.** By ADELBERT RÖSSING (*Zeit. anal. Chem.*, 1897, **36**, 359—369).—The well-known discordance generally observed in the estimation of the total fixed mineral constituents of natural waters, between the results of evaporation and ignition on the one hand, and of estimation of the individual bases and acid radicles on the other, and the disputed question of the effect on this discordance of the ammonium carbonate used by some analysts for recarbonating the alkaline earths causticised by the ignition, induced the author to examine the behaviour of such salts as commonly occur in waters, when evaporated and ignited with ammonium carbonate. Potassium and sodium chloride and sodium sulphate did not alter in weight when repeatedly treated with ammonium carbonate. Calcium and magnesium sulphates both exhibited a considerable loss of sulphuric acid with corresponding decrease in weight. This loss increases on successive treatments, so that the attainment of a constant weight would mislead to a greater extent than the acceptance of the first weighing. The use of an aqueous solution of carbonic anhydride for recarbonating the alkaline earths seems free from error as far as the above-named salts are concerned. When applied, however, to residues containing magnesia, it fails to restore the whole of the lost carbonic anhydride. Mohr's proposal to add a known weight of sodium carbonate to waters containing magnesium chloride fails, therefore, to attain the desired result. The recommendation of Fresenius to convert the whole of the bases into sulphates by evaporation with an excess of sulphuric acid would seem open to a similar objection, since it is necessary to ignite the residue with ammonium carbonate in order to convert the alkali hydrogen sulphates into normal sulphates. Direct experiments show, however, that the loss of sulphuric acid from calcium and magnesium sulphates when solid ammonium carbonate is used is comparatively small, and, for the purposes of water analysis, may be neglected. M. J. S.

**Iodimetric Estimation of Sugars.** By GYSBERT ROMIJN (*Zeit. anal. Chem.*, 1897, **36**, 349—359).—Glucose is oxidised by iodine, in presence of alkali, to gluconic acid with approximate completeness, but if excess of alkali hydroxide is employed the oxidation is too irregular to form the basis of an analytical process. By using borax as the alkali, the reaction, under definite conditions of time, temperature, and dilution, becomes sufficiently regular. The iodine solution recommended contains 40 grams of borax and about 10 grams of iodine per litre. Of this solution, 25 c.c. is mixed with 25 c.c. of the sugar solution containing about 0·15 gram of sugar, in a narrow-necked flask with long glass stopper. The stopper is wired down, and a few drops of water placed in the gutter formed by the stopper and the neck of the flask. The flask is then kept, by means of a thermostat, at 25° for 16—22 hours,

after which the contents are acidified by hydrochloric acid, and the unabsorbed iodine titrated by thiosulphate. For 2 atoms of iodine, 1 molecule of sugar ($C_6H_{12}O_6$) is calculated, and, with glucose, results ranging from 98·6 to 100·9 per cent. were obtained. At greater dilutions, the results were higher, owing to the hydrolytic dissociation of the borax. Very similar results were obtained with the aldoses, galactose, mannose, arabinose, xylose, and rhamnose, whilst levulose, and the ketoses in general, were scarcely attacked, so that the process serves for estimating a sugar of the former class in presence of one of the latter. Sorbose behaves like the ketoses. Maltose, and especially lactose, consume more iodine than dextrose. Saccharose, raffinose, and stachyose, which do not reduce Fehling's solution, are oxidised to a considerable extent by the borax-iodine solution. The process is not applicable to the estimation of sugar in wine or urine, since iodine is consumed by glycerol and by uric acid, as well as by many other substances, such as mannitol, lactic acid, &c. M. J. S.

Volumetric Estimation of Acetone. By Edward R. Squibb. (*J. Amer. Chem. Soc.*, 1896, **18**, 1068—1079).—The process used by the author is a slight modification of the well-known method of Robineau and Rollin, which is based upon the titration of acetone by means of potassium iodide and sodium hypochlorite in an alkaline solution.

The following reagents are required: *A standard solution of acetone.* 50 c.c. of water is put into a flask of 100 c.c. capacity, and carefully weighed; 13 c.c. of pure acetone is added, and the whole is again weighed. The liquid is now transferred to a graduated measuring flask, the weighing flask being well rinsed, and then diluted, so that 10 c.c. contains 0·1 gram of acetone. The author advises keeping this solution in the dark.

*Potassium iodide.*—250 grams of the salt is dissolved in water, and the solution made up to a litre; each c.c. will contain 2·5 grams of the iodide.

*Sodium hydroxide.*—257 grams of commercially pure soda is dissolved in water and the solution made up to 1 litre. When quite clear, 850 c.c. of the solution is poured off and added to the solution of potassium iodide, making 1850 c.c. of total solution.

*Sodium hypochlorite.*—One litre of *liquor sodæ chloratæ*, U.S.P. (containing 2·6 per cent. of available chlorine) is mixed with 25 c.c. of the sodium hydroxide solution.

*Bicarbonated starch solution.*—0·125 gram of starch is ground up with 5 c.c. of cold water, added to 20 c.c. of hot water, and boiled. When cold, 2 grams of sodium hydrogen carbonate is added and stirred until dissolved. This preparation will keep for three months, or longer.

*The titration.*—Ten c.c. of the dilute acetone is put into a 50 c.c. beaker, and 20 c.c. of the mixed soda and potassium iodide solution added; into this, the hypochlorite is rapidly run in from a burette until 8 or 10 c.c. has been added. The iodoform is then allowed to settle, and a few drops more of the hypochlorite added. Should this produce a dense cloudiness, a little more is added, until finally the cloudiness is only very slight. It is then tested by starch, a drop of the

starch solution being placed near to a drop of the liquid on a white porcelain plate, and the two drops run into one another. If no blue colour is visible, a few more tenths of a c.c. of hypochlorite solution is run in, repeating the process until the starch gives a blue coloration. Having now checked the standard solution, any number of acetone estimations may be made, but it must be remembered that the hypochlorite does not keep, and must, therefore, be standardised daily. It is also advisable, when dealing with acetone solutions of unknown strength, that the estimation should be repeated, taking such a quantity of solution that the amount of acetone is about the same as that used in the check experiment.

The author also confirms the statement that the presence of ethylic alcohol does not interfere with this process, although it is an iodoform yielding substance. L. DE K.

**Estimation of Acetone in Urine.** By G. ARGENSON (*Bull. Soc. Chim.*, 1897, [iii], 15, 1055—1058).—Léoben's method of determining acetone in urine consists in distilling the liquid until a fourth part has passed over, converting the acetone into iodoform, decomposing the latter with alcoholic potash, and determining the potassium iodide by means of a standard solution of silver nitrate. Numerous experiments having shown that the quantity of iodoform produced is invariably smaller than that required by the equation

$$COMe_2 + 3I_2 + 4KOH = CHI_3 + CH_3 \cdot COOK + 3KI + 3H_2O,$$

and depends largely, moreover, on experimental conditions, the author has elaborated a table which supplies the weight of acetone per litre, corresponding with the volume of silver nitrate employed. The conditions for which this table holds good are clearly laid down.

M. O. F.

**Extension of Legal's Reaction to Compounds containing the Acetyl Group, and their Derivatives.** By GEORGES DENIGÈS (*Bull. Soc. Chim.*, 1897, [iii], 15, 1058—1064).—Legal's test for acetone consists in adding to the liquid a few drops of a solution of sodium nitroprusside, followed by a caustic alkali; a red coloration is produced, and gradually diminishes, but deepens to carmine on treatment with excess of glacial acetic acid.

The author has made the following generalisations concerning this change. (1) All those compounds which give Legal's reaction contain the acetic group, the carbonyl radicle being combined with either hydrogen or a hydrocarbon residue. (2) Compounds containing an acetyl or substituted acetyl complex do not give Legal's reaction if the carbonyl radicle is united to the groups OH, OR, OM (acetates), $NH_2$, or to chlorine, these substances developing, on the other hand, a red coloration with ferric chloride. (3) Those compounds which contain an acetyl group of which the carbonyl radicle is combined with an aromatic hydrocarbon give rise to a blue coloration when submitted to Legal's test.

Acetylphenylhydrazine, and hydrazine derivatives generally, must be excluded from the second of the above generalisations. These substances do give Legal's reaction, but the coloration produced differs from the ordinary one in being transformed into violet by hydrochloric acid instead of being destroyed. M. O. F.

**Colour Reactions of the Aldehydes and Ketones.** By BÉLA VON BITTÓ (*Zeit. anal. Chem.*, 1897, **36**, 369—376).—Compounds of the aldehyde or ketone class, in which the formyl or carbonyl group is not combined with a completely substituted hydrocarbon, give, with salts of the metadiamines, either immediately or in the course of an hour or two, deeply coloured solutions with intense green fluorescence. Ortho- and para-diamines also give colour reactions, but without any marked fluorescence. To obtain the reaction, a few c.c. of a 0·5—1 per cent. solution of the metadiamine hydrochloride is added to the aqueous or alcoholic solution of the substance to be tested. Alkalis destroy the colour, which returns on acidifying. Mineral acids, with the exception of metaphosphoric acid, enfeeble the colour. The reaction occurs with aromatic aldehydes, whether the formyl is united directly with a benzene residue or through the intermediary of a fatty alkyl. The reaction is not exhibited by the mixed ketones or by the ketonic acids. The colour produced is in most cases yellow to orange, but cinnamaldehyde gives a cherry-red, and diethyl ketone a violet-red.

The author has also studied the behaviour of Schiff's reagent (a 0·025 per cent. solution of magenta decolorised by passing sulphurous anhydride through it (compare this vol., ii, 235) with a number of aldehydes and ketones. The violet colour is produced by all the aldehydes of the fatty series, and by fatty ketones in which the carbonyl is united with at least one methyl group. It is not produced either by monochloracetone or by diethyl ketone, or by the mixed ketones or ketonic acids. Cinnamaldehyde, and similar compounds, give a yellow coloration, subsequently passing into violet. Schiff's reagent, when boiled and cooled, always acquires a bluish-violet colour, which unfits it for the above reactions. It ought, therefore, never to be heated. M. J. S.

**Analysis of Wheat.** By AIMÉ GIRARD (*Compt. rend.*, 1897, **124**, 876—882, 926—932).—See this vol., ii, 382 and 425.

**Hæmochromogen as a Test for Blood.** By ZAKARIÁS DONOGÁNY (*Virchow's Archiv*, 1897, **148**, 234—235).—The most delicate test, of those investigated, for the purpose of detecting blood in urine, fæces, sputum, &c., is the preparation of hæmochromogen crystals, and the spectroscopic examination of the orange-red solution which they form. These are best obtained by adding pyridine to the suspected fluid, previously rendered alkaline with ammonium sulphide, or, better, with sodium hydroxide. W. D. H.

**The Uncertainty of the Guaiacum Reaction for Active Diastase.** By BRONISLAW PAWLEWSKI (*Ber.*, 1897, **30**, 1313—1314).—The author considers the guaiacum reaction to be very uncertain; not only does this reagent give a similar colour with peptone, gelatin, albumin, &c., but even on addition of hydrogen peroxide to the tincture a blue colour is produced. The test is much better suited for the detection of nitrous acid, a deep blue coloration being instantly formed in solutions containing as little as 0·00005 gram of a nitrite.

J. F. T.

## General and Physical Chemistry.

**Examination of some Spectra.** By Paul Émile Lecoq de Boisbaudran (*Compt. rend.*, 1897, **124**, 1419—1421).—The author replies to certain criticisms of Eder and Valenta on his description of the spectra of gold and gold chloride, and maintains the accuracy of his former statements. C. H. B.

**Iron Lines present in the Hottest Stars.** By Joseph Norman Lockyer (*Proc. Roy. Soc.*, 1897, **60**, 475—476).—On a former occasion, the author observed that in the case of iron, two lines in the visible spectrum at 4924·1 and 5018·6 on Rowland's scale, were greatly enhanced in brightness on passing from the arc to the spark. Seven additional lines have been found whose brightness is enhanced at the highest temperature. It appears probable that, in a space heated to the temperature of the hottest spark, and shielded from a lower temperature, these lines would constitute the spectrum of iron. In the hottest stars, iron is practically represented by the enhanced lines alone; those which build up, for the most part, the arc spectrum are almost or entirely absent. But the enhanced lines may be absent from the spectrum of a star, either on account of too low or too high a temperature. In the case of low temperature, iron is represented among the lines in the spectrum, but at the highest temperature all visible indications of its presence seem to have vanished. H. C.

**Absorption of Ultra-violet Rays by Gases and Liquids.** By J. Pauer (*Ann. Phys. Chem.*, 1897, [ii], **61**, 363—379).—Compare this vol., ii, 393.

**Colour of the Phosphorescence of Strontium Sulphide.** By José Rodriguez Mourelo (*Compt. rend.*, 1897, **124**, 1521—1523).—The colour of the phosphorescence of strontium sulphide is always bluish-green, the hue being most nearly pure green when the sulphide has been prepared by the author's modification of Verneuil's method (this vol., ii, 450). The intensity of the phosphorescence depends on the composition and physical condition of the sulphide, and is not directly affected either by the temperature at which it is heated or by the duration of the heating. It is noteworthy that the most intensely fluorescent variety need not be heated more than three hours, and that an excessively high temperature is not necessary. Nothing is gained by prolonging the heating for several hours beyond the time necessary to gain the maximum effect either with this variety or with those prepared in other ways. C. H. B.

**Behaviour of Minerals with the X-Rays.** By Cornelius Doelter (*Jahrb. f. Min.*, 1897, i, 256—257. Compare this vol., ii, 45).—Using the methods previously described, the transparency of some more minerals for the Röntgen X-rays are compared. Phenakite is one of the most transparent of minerals, and is placed in the author's

group II. Olivine, tourmaline, biotite, zoisite, and sphene have about the same transparency as calcite (Group VI.). Sapphire seems to be more transparent than ruby, and aquamarine is more transparent than the darker coloured emerald. L. J. S.

**Refractive Powers of Mixtures of Two Liquids.** By F. ZECCHINI (*Gazzetta*, 1897, **27**, i, 358—383).—The author has examined the relation between the refractive power and the density of mixtures of ethylic alcohol and carbon bisulphide, ethylic alcohol and $\alpha$-bromonaphthalene, ethylic alcohol and cinnamaldehyde, phenylic thiocyanate and carbon bisulphide, cinnamaldehyde and carbon bisulphide, $\alpha$-bromonaphthalene and carbon bisulphide, and of anethoil and carbon bisulphide, in a similar manner to Pulfrich (*Zeit. physikal. Chem.*, **4**, 562), and Buchkremer (Abstr., 1891, 2). Using the nomenclature adopted by the latter, the author writes the equations $(N-N_v)/N=a(D-D_v)/D$ and $(D-D_v)/D=c$ in the form $N_v(1-ac)(p_1+p_2)\div D(1-c)=N_1p_1/d_1+N_2p_2/d_2$ in which $v_1$ is the volume of one of the constituent liquids of density $d_1=p_1/v_1$, and refractive index $N_1$ whilst $v_2$ is the volume of the other constituent liquid of density $d_2=p_2/v_2$ and refractive index $N_2$; when $a=1$ or $c=o$, the equation becomes $N(p_1+p_2)/D=N_1p_1/d_1+N_2p_2/d_2$.

The author fully confirms the conclusions of Pulfrich and of Buchkremer (*loc. cit.*), and notes that when the value $(1-ac)/(1-c)$ differs little from unity, the rule cannot be experimentally verified.

W. J. P.

**Use of Aldehydes and Ketones in the Presence of Sodium Sulphite for Developing the Latent Photographic Image.** By AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1164—1169).—It is well known that formaldehyde, when added to an organic developer, considerably increases the reducing power of the developer; and the authors show that other aldehydes and also ketones exhibit the same property. The aldehyde or ketone, however, will not act by itself, but requires the presence of sodium sulphite; the sulphite cannot be replaced by other alkali salts such as sodium acetate or phosphate. The same compounds not only accelerate development but, in the presence of sodium sulphite and a phenolic developer, also bring out the latent image without the use of alkali. The authors suppose that in the presence of the phenolic developer the sodium sulphite is, to some extent, decomposed into free alkali which combines with the phenol and into sodium hydrogen sulphite which combines with the aldehyde or ketone. This view is supported by experimental results.

It is found that the best results are given by pyrogallol, sodium sulphite, water, and acetone. The best developing mixture in the case of quinol is water (100 grams), quinol (3 grams), sodium sulphite (10 grams), and acetone (10 c.c.). J. J. S.

**Photo-electric Phenomena and Photographic Processes.** By H. LUGGIN (*Zeit. physikal. Chem.*, 1897, **23**, 577—635).—The author exposed to light a sensitive electrode similar to that previously described (Abstr., 1894, ii, 405), but which could be raised to any

definite potential above that of the liquid. The current produced or the photo-current was measured, and it was found that an intimate connection exists between the strength of the photo-current and the depth of the darkening of the sensitive electrode. As the potential of the electrode is increased, however, the photo-current decreases, and ultimately a potential is reached where the current becomes zero and by increased exposure may pass over to a current of opposite sign. Where the action of the current is to remove the halogen and hence cause darkening of the electrode, the current is called normal or positive, currents which act in the reverse sense being known as *solarisation current*, and experiments show that both kinds of current may be produced with the same electrode, according to its potential and the light intensity. The solarisation current, in the case of silver chloride electrodes, more readily occurs with yellow light, whilst, on the other hand, blue light favours the production of the normal current, which, in contradistinction to the solarisation current, is coterminous with the exposure. The potential at which no normal current is produced is known as the equilibrium potential, and a linear equation is found to hold for the relation of the photo-current to the defect from the equilibrium potential, and in the equation the constant is probably dependent on the dissociation of the silver salt. The author endeavours to connect these results with the purely photographic phenomena, and considers that solarisation appearances are intimately and causally connected with the solarisation current, and at any rate with printing out papers the connection between the photo-electric and photographic phenomena is in the author's opinion established. The applicability of the halogen salts appears also to be connected with the value of the equilibrium potential, and the author finally discusses at some length the production of images by development. L. M. J.

**Thermal Conductivity and Ion Motion.** By Georg Bredig (*Zeit. physikal. Chem.*, 1897, **23**, 545—546).—Jäger has shown that the thermal conductivity of a salt solution is given by the expression $k = k'(1 - ap)$ where $k'$ is the conductivity of water, $p$ the percentage of salt in the solution, and $a$, a specific constant. By making $k' = 100$ and $p = 100$ the expression $k = 100 - a10^4$ is obtained, and if this is multiplied by the equivalent weight, the result is what the author terms the equivalent conductivity. Jäger's numbers are employed, and show that, like the electrical conductivity, this constant also is an additive property of the ions. L. M. J.

**Distribution of a Current among the Ions in a Solution.** By Ed. v. Stackelberg (*Zeit. physikal. Chem.*, 1897, **23**, 493—496).—In the case of a solution containing many ions, the author deduces for (1) the total current, and (2) the portion conveyed by each set of ions the expressions:—(1), $E = C(N_a u_a + N_b u_b + \ldots N_m u_m + \ldots)$ and (2) $\Delta N_a = E \cdot N_a u_a / \Sigma(Nu)$, where $N_a$, &c., . . . are the number of gram equivalents of the free kations, $N_m$ . . . the number of gram equivalents of the anions, and $u_a$ . . . their respective migration velocities.

L. M. J.

**Electrolytic Dissociation in Acetone Solution.** By Giacomo Carrara (*Gazzetta*, 1897, i, 207—222).—The author notes that

Zelinsky and Krapiwin (this vol., ii, 5) have ignored his previous work (Abstr., 1896, ii, 511) on electrolytic dissociation in methylic alcohol solution, and claims priority as against Laszczynski (*Zeit. f. Elektrotec. u. Elektrochem.*, 1895, 55), certain of the results arrived at by the latter having been previously deduced by the author (Abstr., 1894, ii, 310; 1895, ii, 302).

Using a carefully purified sample of acetone, boiling at 56·3° under 761·4 mm. pressure, and having a conductivity of $\mu = 0{\cdot}00066$ to $0{\cdot}0010$ at 25°, the author has determined the electrical conductivity of solutions of various electrolytes in acetone solution; the values obtained are

| Electrolyte. | Acetone. | | Water. | Methylic Alcohol. |
|---|---|---|---|---|
| | $v$ | $\mu_v$ | $\mu_\infty$ | $\mu_\infty$ |
| LiCl | 1024 | 33·42 | 110 | 77·3 |
| KI | 2048 | 153·6 | 142·6 | 97·63 |
| NaI | 1024 | 139·85 | 121·4 | 89·77 |
| $NH_4I$ | ∞ | 152·5 | 142·6 | 105·25 |
| $NMe_4I$ | 2692 | 119·76 | 115·6 | 115·3 |
| $NEt_4I$ | 2048 | 111·04 | 199·2 | 91·13 |
| $SMe_3I$ | 2048 | 117·49 | 119·3 | 119·68 |
| $SEt_3I$ | ∞ | 167 | 107·6 | 112·53 |
| HCl | 63·55 | 2·21 | 395·2 | 133·08 |
| $CCl_3{\cdot}COOH$ | 46·48 | 0·419 | 358 | 121·48 |

summarised in the accompanying table, those given previously (Abstr., 1806, ii, 511) for aqueous and methylic alcohol solutions being also quoted to assist comparison.

Potassium and sodium iodides are the only salts used of which the molecular conductivities in acetone solution change on dilution in such a way as to approximate to a limiting value; with ammonium iodide, there seems a tendency for the conductivity to change normally with dilution, but for the other electrolytes examined the increase of molecular conductivity, which attends a doubling of the volume, increases, instead of decreasing, as the dilution increases. This kind of behaviour has also been observed by Laszczynski (*loc. cit.*) with acetone solutions of mercuric chloride, silver nitrate, and sodium thiocyanate. It is noteworthy that hydrogen chloride, trichloracetic acid, and lithium chloride, hygroscopic substances, although highly dissociated in aqueous solution, give very low electrical conductivities in acetone; the low values may be due, in the case of lithium chloride, to combination with the solvent. The electrical conductivity of a solution depends (*a*) on the dissociating power of the solvent and (*b*) on the "electrolytic friction" or friction between the solvent and the ions. These two factors seem, in the case of aqueous solutions, to operate in the same direction on the molecular conductivity, that is to say, whilst the actual dissociating power is great, the friction is small. In acetone solutions, however, the solvent seems to possess but slight dissociating power, and at the same time interposes but slight electrolytic friction,

so that the velocity of ionic migration is great. The small dissociating power of acetone is well shown by comparing the number of litres ($n$) in which a given quantity of an electrolyte must be dissolved in order that the degree of dissociation ($d$) shall be the same in the various solvents dealt with. Thus, when $d$ is 0·760 for triethylsulphine iodide, $n$ is 8 with water as the solvent, 39 with methylic alcohol, 504 with ethylic alcohol, 1015 with propylic alcohol, 89 with allylic alcohol, and 498 with acetone. Again, when $d$ is 0·920 for potassium iodide, $n$ is 24 for water as the solvent, 436 for methylic alcohol, and 512 for acetone.

W. J. P.

**Electrolytic Dissociation of Methylic Alcohol and of Water dissolved in it.** By GIACOMO CARRARA (*Gazzetta*, 1897, **27**, i, 422—440. Compare Abstr., 1896, ii, 511).—The author carefully purified methylic alcohol by dehydration with copper sulphate and barium oxide, subsequently distilled it from a few pellets of sodium, and then distilled it under 20 mm. pressure from 2 per cent. of phosphoric anhydride. The electrical conductivity of the sample thus obtained was determined by Kohlrausch's method, the alcohol being distilled into the flask containing the electrodes; a large number of determinations were made under various conditions, and as the end result the author states the electrical conductivity of methylic alcohol to be $0·072 \times 10^{-10}$ at 25°, a much smaller value than that given by Völlmer (*Ann. Phys. Chem.*, **52**, 348), namely $1·22 \times 10^{-10}$, which is the smallest value previously recorded.

It is concluded that methylic alcohol is partially dissociated and about twice as much so as water; 1 gram-molecule of methylic alcohol is dissociated in about 5·5 million litres at 25°. The electrical conductivity of methylic alcohol is not affected by the addition of 0·23 per cent. of benzene, but falls to about two-thirds on adding 0·71 per cent. of benzene; the electrical conductivity of the alcohol is thus due to the presence of an electrolyte which, in accordance with the general rule, has a lower conductivity in a mixture of solvents.

It is further shown that water is dissociated in methylic alcohol solution, and in very dilute solutions the ionic concentration is proportional to the square root of the total concentration of the water. In very dilute solutions, the dissociation of the water is always rather greater than the electrolytic dissociation of water in aqueous solution; that dilute solutions of water in ethylic alcohol show the contrary effect to this is probably due to the much less considerable dissociating power of ethylic alcohol.

W. J. P.

**The Chemical Action of Electrical Oscillations. II.** By ALEXANDER DE HEMPTINNE (*Zeit. physikal. Chem.*, 1897, **23**, 483—492).—In order to ascertain the effect of the wave-length, the author determined the maximum pressure at which the tube became luminous when subjected to the influence of the oscillation, investigating the cases of tubes with allylic alcohol, acetone, propylic aldehyde, methylic alcohol, and ethylic alcohol. Of these, the two last showed a marked increase of sensitiveness as the wave-length increased, but, in the other cases, the pressure remained almost constant except for acetone, where a maximum of sensitiveness was obtained in the middle of the series.

The author describes an experiment illustrating the metallic conductivity of a glowing tube, and points out that from the analogy to metals, the chemical action would be expected to vary with the wave-length. According to Ebert, the spectra of vapours vary with the wave-length, but, although the author also finds a slight variation in the compounds examined, he points out that this may be due to decomposition and the formation of new products; the influence on the spectrum of the substance itself, therefore, is doubtful. In general, the sensitiveness increases with the molecular weight, but it is dependent also on other data, thus ethylic ether is less sensitive than acetone. Temperature has also a marked effect, but its complete investigation was postponed; a magnetic field appeared to have no influence. L. M. J.

**Variation with Temperature of the Transference Ratios of Cadmium in Aqueous Solutions.** By VICTOR GORDON (*Zeit. physikal. Chem.*, 1897, **23**, 469—482).—The electromotive force of the element –Cd | $CdSO_4$aq. | | $CuSO_4$aq. | Cu– increases with temperature, indicating a diminution in the concentration of the cadmium ions, which may be due to the formation of molecular aggregates, these having been proved to exist in the case of the halogen cadmium salts. On this assumption, the transference ratio should not be greater at high than at low temperatures; the author determined this value at different temperatures, that is, the ratio of the weight of cadmium which has actually passed from the anode liquid, to the quantity deposited on the cathode, or dissolved from the anode. The values obtained were (1) 11·56 per cent. cadmium sulphate, 10° - 0·328; 40° – 0·283; 80° – 0·281. (2) 34·8 per cent. solution, 10° – 0·197; 40° – 0·190; 70° – 0·203. With cadmium iodide, negative values were obtained which were independent of temperature. L. M. J.

**Electrical Resistivity of Electrolytic Bismuth at Low Temperatures and in Magnetic Fields.** By JAMES DEWAR and JOHN AMBROSE FLEMING (*Proc. Roy. Soc.*, 1897, **60**, 425—432).—The authors have extended their observations (this vol., ii, 240) on the behaviour of electrolytically prepared bismuth, when cooled to very low temperatures and at the same time subjected to transverse magnetisation. The electrical resistivity of bismuth in C.G.S. units, transversely magnetised in a constant magnetic field, but at variable temperatures, is given in the following table:—

| Temperature of the bismuth wire. | Out of the magnetic field. | In the magnetic field. | | |
|---|---|---|---|---|
| | | Strength 2,450 C.G.S. units. | Strength 5,500 C.G.S. units. | Strength 14,200 C.G.S. units. |
| + 19° | 116,200 | 123,500 | 132,000 | 187,000 |
| – 79 | 78,300 | 105,000 | 158,000 | 284,000 |
| – 185 | 41,000 | 186,000 | 419,000 | 1,740,000 |
| – 203 | 34,300 | 283,500 | — | — |

It will be seen that if the transverse field is zero, cooling the bismuth always reduces its resistance. If, then, the bismuth is transversely magnetised, the resistance is increased, and for every temperature below the normal one, there is some particular strength of transverse field, which just annuls the effect of cooling, and brings the resistance of the bismuth back again to the same value it had when not cooled and when not in any magnetic field. The lower the temperature, the less is the strength of field which will bring the bismuth back to its original resistance when not cooled and not in the field.

These results indicate that at absolute zero bismuth should be converted into a non-conductor by a sufficiently strong transverse magnetisation. In this respect, bismuth is a remarkable exception to other metals.

The effect of transverse magnetisation at low temperatures was tried on zinc, iron, and nickel, but no effect was found sensibly greater at low than at ordinary temperatures, although these metals have their resistance affected by magnetisation to a small degree. At a temperature of about 150°, bismuth would probably cease to have its resistivity affected by a transverse magnetic field. H. C.

**Dieletric Constant of Ice and Alcohol at very Low Temperatures.** By JAMES DEWAR and JOHN AMBROSE FLEMING (*Proc Roy. Soc.*, 1897, **61**, 2—18).—The dielectric constant of ice is found to increase progressively from a value of about 2·8 to 11·6 between the limits $-198°$ and $-131°$ of the platinum thermometer. At absolute zero, the dielectric constant would probably not be far from 2·0. With relatively very slow reversals of electromotive force, the dielectric constant of ice at $-185°$ is a number not far from 2·9, which is not very different from that found by observers using reversals of many millions per second by the use of electrical oscillations or waves, when working at temperatures of 0° or a little below. On the other hand, the values found for ice at or a little below 0°, when using very slow oscillations, seems to indicate a dielectric constant of 78. It remains to be seen how the high value is connected with the low one, and whether this variation may be properly regarded as a case of anomalous dispersion.

The dielectric constant of solid alcohol at $-185°$ was found to be 3·12. The dielectric resistance of ice and frozen alcohol at and from the temperature $-185°$ was taken. With rising temperature, a rapid increase takes place in the conductivity of ice at about $-90°$, and in the case of alcohol as soon as a rise in temperature of about 10° has occurred, the conductivity begins to go up with great rapidity.

H. C.

**Development of Heat by the Action of Bromine on Unsaturated Compounds.**—By WLADIMIR F. LUGININ and IVAN KLABUKOFF (*Compt. rend.*, 1897, **124**, 1303—1306).—The authors have determined directly in the calorimeter the quantity of heat developed by the action of bromine on various allyl and allied derivatives in presence of carbon tetrachloride or alcohol. The results are as follows: Diallyl, 56,114 Cal. ($2 \times 28{,}057$); allylic chloride, 26,821; allylic bromide, 26,695; allylic alcohol, 27,732; allylic ether, 27,017

allylic acetate, 28,133; cinnamic alcohol, 22,321; crotonaldehyde, 19,349; and mesitylic oxide, 20,238. It is noteworthy that in the case of allylic alcohol and its derivatives the values are almost the same, and in the case of the bromide and chloride are practically identical. The substitution of phenyl for hydrogen in allylic alcohol reduces the heat developed by the action of bromine, and the presence of the ketonic or aldehydic function has a similar effect.

C. H. B.

**Cryoscopic Observations on Acid Amides.** By KARL AUWERS (*Zeit. physikal. Chem.*, 1897, **23**, 449—468).—The cryoscopic relations in naphthalene and benzene solutions were investigated for a large number of derivatives of aniline and its homologues, such as the anilides, and their halogen, nitro-, and alkyloxy-derivatives. Aniline, toluidine, anisidine, and the nitranilines all behaved normally, but abnormal values were obtained for most of the other compounds. In the anilides of the fatty acids, the molecular weight of the acid radicle has but little influence on the abnormality, the greatest deviation from normal values occurring with acetanilide. The general rules found by Innes and Orton as applying to the substituted phenols hold also for the compounds examined, that is, an ortho-substituent diminishes the abnormality, which is, however, in general increased by a para-group, and to a less extent by a meta-group. The acetyl compounds are in general more abnormal than the formyl compounds. The nitro-group has a powerful normalising influence in the ortho-position, but does not exert any abnormalising effect in the para-position; the normalising influence of methoxyl and the aldehyde group in the ortho-position is very marked. L. M. J.

**Maximum Depression of the Freezing Point of Mixtures.** By EMANUELE PATERNÓ and G. AMPOLA (*Gazzetta*, 1897, **27**, i, 481—536).—The authors have determined the freezing points of long series of mixtures of a number of pairs of organic compounds and find that in all the cases examined the freezing points of the mixtures are lower than those of the constituents of the mixture. The maximum depressions of the freezing points are given in the accompanying table, in which columns 1 and 3 state the components of the mixture and columns 2 and 4 give their respective melting points; column 5 states the percentage of the component named in column 1 in the mixture of lowest freezing point, and column 6 gives the melting point of the latter. Mixtures of thymol and trimethylcarbinol or water, and of benzene and paraldehyde were also examined, and conform to the general rule. Usually, the curve obtained by plotting freezing point against composition shows only one minimum, but in the case of mixtures of trimethylcarbinol and phenol it shows five. The minimum freezing point never corresponds with a mixture containing any definite proportion, and the freezing points of the mixtures cannot be even approximately calculated by Ostwald's method, which depends on the application of Van't Hoff's formula $\Delta = 2T^2/100\lambda$. In some cases, two definite freezing points for the eutectic mixture are obtained and frequently the minimum freezing point is lower than that of the eutectic mixture; the authors, although considering their results as

| 1. | 2. | 3. | 4. | 5. | 6. |
|---|---|---|---|---|---|
| $C_6H_6$ .................... | 5·53° | $pC_6H_4Me_2$ | 13·35° | 55·22° | −22·39° |
| ,, .................... | 5·55 | $C_6H_5OH$ | 40·24 | 59·13 | −5·275 |
| ,, .................... | 5·48 | $pC_6H_4BrMe$ | 26·71 | 50·25 | −16·78 |
| $pC_6H_4Me_2$ .............. | 13·35 | ,, | 26·74 | 60·78 | 2·39 |
| $C_6H_5\cdot OH$ .............. | 40·06 | ,, | ,, | 42·76 | 13·41 |
| Thymol.................. | 49·20 | ,, | ,, | 35·51 | 11·35 |
| $C_2H_4Br_2$ ... .......... | 9·91 | ,, | ,, | 57·87 | −6·67 |
| $CMe_3\cdot OH$ ............... | 23·52 | ,, | ,, | 61·15 | 8·76 |
| $C_2H_4(CO)_2NEt$ ....... | 28·81 | ,, | 26·73 | 55·15 | 0·54 |
| $(CH_2Ph)_3N$ ......... . | 91·3 | ,, | ,, | 30·97 | 14·19 |
| Veratrole ............... | 22·22 | ,, | ,, | 47·36 | −3·33 |
| $C_2H_4Br_2$.................. | 10·00 | $pC_6H_4Me_2$ | 13·35 | 67·26 | −18·85 |
| Paraldehyde ............ | 11·24 | ,, | ,, | 38·10 | −14·14 |
| $C_6H_5\cdot OH$ .............. | 40·24 | ,, | ,, | 37·04 | 5·575 |
| Veratroie ...... ........ | 22·40 | ,, | ,, | 51·01 | −4·0 |
| $CH_3\cdot COOH$ ............ | 15·05 | ,, | ,, | 48·53 | 0·17 |
| $C_2H_4(CO)_2NEt$ ......... | 28·81 | ,, | 13·28 | 63·72 | −2·63 |
| Paraldehyde ............ | 12·03 | $C_2H_4Br_2$ | 10·00 | 43·15 | −17·20 |
| $C_6H_5\cdot OH$ ............... | 40·24 | ,, | ,, | 21·50 | −1·32 |
| ,, .............. | ,, | $CH_2Ph_2$ | 24·45 | 39·16 | 10·01 |
| ,, .............. | ,, | ,, | 24·68 | 38·68 | 11·52 |
| Thymol.................. | 49·24 | $C_6H_5\cdot OH$ | 39·53 | 48·17 | 7·47 |
| $CMe_3\cdot OH$ ............... | 24·95 | ,, | 40·87 | 82·90 | 9·65 |
| ,, .............. | ,, | ,, | ,, | 69·87 | 19·95 |
| Thymol.................. | 49·32 | $CH_3\cdot COOH$ | 15·05 | 56·27 | −8·76 |

merely preliminary, do not think that this curious observation is due to experimental error. W. J. P.

**Abnormal Freezing Point Depressions.** By FELICE GARELLI (*Gazzetta*, 1897, 27, i, 247—254).—The author combats Bodländer's criticisms (this vol., ii, 133) respecting his conclusions. (This vol., ii, 14). W. J. P.

**Cryohydrates.** By GIUSEPPE BRUNI (*Gazzetta*, 1897, 27, i, 537—561).—The author gives a short summary of our knowledge of cryohydrates, and has experimentally investigated a number of cases; he determines the melting point of a cryohydrate by allowing it to freeze round a thermometer bulb and noting the temperature at which the thermometer remains stationary. The cryohydrate is prepared by taking a solution slightly more concentrated than that corresponding in composition with the cryohydrate, cooling it to the cryohydric temperature and dropping in crystals of ice and of the salt; the deposited cryohydrate is separated, melted, and again frozen as before in order to obtain material which has the cryoscopic composition, and is suitable for analysis.

Mixtures of the double salt, $ZnSO_4,K_2SO_4 + 6H_2O$, with excess of zinc sulphate give a cryohydric temperature of −6·6°, and with excess of potassium sulphate of −1·7°; the cryohydric temperature of zinc sulphate is −6·4° and the cryohydrate contains 43·5 per cent. of $ZnSO_4$; the cryohydric temperature of potassium sulphate is −1·55°, the cryohydrate containing 7·4 per cent. of potassium sulphate, whilst the cryohydric temperature of the double salt is −1·0°, and the cryo-

hydric composition is 9·8 per cent. of $ZnSO_4,K_2SO_4$. The cryohydric solutions of mixtures of the double salt with one of its constituent salts have lower freezing points than the cryoscopic solution of the double salt or of the component salt present in excess.

By examining the isomorphous salts, zinc sulphate and magnesium sulphate, the author shows that the cryohydric temperature of a solution in equilibrium with mixtures of two perfectly isomorphous salts varies as the composition of the mixture of salts, the limits being the cryohydric temperatures of the single salts. Thus the cryohydric temperatures of mixtures of magnesium and zinc sulphates containing 100, 69·5, 58·8, 37·5, 19·6, and 0 per cent. of $MgSO_4$ are $-5·2°$, $-5·5°$, $-5·5°$, $-6·0°$, $-6·2°$, and $-6·4°$ respectively.

The case of mixtures of three salts which are not isomorphous and do not form double salts was also examined, the salts selected being potassium chloride, nitrate, and sulphate. The accompanying table

| Salts present. | | | Cryohydric temperature. | Composition of cryohydrate. | | |
|---|---|---|---|---|---|---|
| A. | B. | C. | | A. | B. | C. |
| KCl | — | — | −10·8° | 24·9 | 0 | 0 |
| — | $KNO_3$ | — | −2·85 | 0 | *12·6* | 0 |
| — | — | $K_2SO_4$ | −1·55 | 0 | 0 | 7·4 |
| KCl | $KNO_3$ | — | −11·5 | *24·5* | *4·5* | 0 |
| KCl | — | $K_2SO_4$ | −10·9 | *24·2* | 0 | *1·4* |
| — | $KNO_3$ | $K_2SO_4$ | −3·3 | 0 | 9·1 | 5·2 |
| KCl | $KNO_3$ | $K_2SO_4$ | −11·55 | 24·5 | 4·5 | 1·3 |

summarises the results, the concentrations being expressed in parts by weight of salt per 100 of water; the numbers quoted in italics are those obtained by other workers. It follows that the cryohydric temperature of a solution in equilibrium with three non-isomorphous salts which do not form double salts is lower than the cryohydric temperatures of solutions in equilibrium with either two of the three salts.

W. J. P.

**Molecular Volumes of Crystallised Carbohydrates.** By JOSEPH PIONCHON (*Compt. rend.*, 1897, **124**, 1523—1524).—See this vol., i, p. 547.

**Extension of the Law of Avogadro to Homogeneous Liquids.** By ISIDOR TRAUBE (*Ann. Phys. Chem.*, 1897, [ii], **61**, 396—400).—As the author has shown in previous communications, the molecular covolumes of homogeneous liquids are the same under similar conditions. Where exceptions to this rule are met with, they may be either traced to association in the liquids examined or to the influence of changes in the sphere of vibration of the atoms as shown by the refractions of the liquids (compare Abstr., 1896, ii, 235; and this vol., ii, 85).

H. C.

**Solubility of Super-cooled Liquids.** By LUDWIG BRUNER. (*Zeit. physikal. Chem.*, 1897, **23**, 542—544).—The solubility of an

over-cooled liquid cannot be identical with that of the solid, or two systems not in equilibrium with one another could be in equilibrium with a third system, and the author describes experiments proving the greater solubility of the liquid in cases where no water of crystallisation is present to affect the result. A hot saturated solution of hydrocinnamic acid is made and cooled, the acid separating in drops which remain liquid at ordinary temperatures; after the solution has been filtered from the drops of liquid acid, the introduction of a crystal of the solid acid or violent agitation causes the filtrate to crystallise; the solution saturated with respect to the liquid acid is supersaturated, therefore, with respect to the solid. Measurement with alkali showed the solubility of the liquid to be greater in the ratio 15 : 17. In super-cooled solutions of thymol also, the solidification of the liquid thymol below the water is immediately followed by the separation of crystals throughout the solution. Analogous results had been obtained by Alexéeff with salicylic and benzoic acids, which he had explained by the assumption of "isomeric solutions." L. M. J.

**Velocity of Dissolution of a Solid in its own Solution.** By Arthur Amos Noyes and Willis Rodney Whitney (*Zeit. physikal. Chem.*, 1897, **23**, 689—692).—In order to prevent any noticeable alteration of surface during the experiments, the solids were compressed into cylinders about 8 cm. long and 2 cm. in diameter. These were introduced into water, and the concentration determined from time to time. Experiments were performed with benzoic acid and lead chloride, and the dissolution-velocity was found to be given by the equation $dx/dt = C(S - x)$ where $x$ is the concentration of the solution and $S$ that of the saturated solution, $C$ being a constant. The author considers the equation to really be that of diffusion, the film of liquid immediately in contact with the solid being a saturated solution which diffuses into the more dilute layers. L. M. J.

**Solubility of Mixed Crystals and Magnitude of the Crystal Molecule.** By Andreas Fock (*Zeit. Kryst. Min.*, 1897, **28**, 337—413). —Van't Hoff has indicated that isomorphous mixtures or mixed crystals may be regarded as solid solutions; solid solutions must thus be treated as molecular mixtures. Roozeboom (Abstr., 1892, 265), by applying the theory of thermodynamical potential, showed that in the equilibrium condition at constant temperature and pressure, to each solid solution or isomorphous mixture of two substances corresponds a perfectly definite concentration of the two constituents in the liquid solution. It was then shown by Nernst (Abstr., 1890, 3) that his principle respecting the partitioning of a dissolved substance between two non-miscible solvents in equilibrium is applicable to the case of a solid solution in equilibrium with a liquid solution.

Let $c_1$ and $c_2$ be the number of gram-molecules per unit volume of two isomorphous salts, $A$ and $B$, in a common liquid solution and $x_1$ and $x_2$ be the corresponding molecular concentrations in the solid solution of $A$ and $B$ with which equilibrium is established; then the partition coefficients $c_1/x_1$ and $c_2/x_2$ are in general constant and independent of the absolute concentration. If, however, the molecular weights are $n$ times as great in the liquid as in the solid solutions, then it follows

from the law of mass-action that the ratios $c_1/x_1^{\frac{1}{n}}$ and $c_2/x_2^{\frac{1}{n}}$ or $c_1^n/x_1$ and $c_2^n/x_2$, where $n$ is greater or less than unity, will be constant. These simple laws can only be expected to hold in dilute solutions, the gaseous laws not being applicable to concentrated solutions; further, in dilute solutions, the electrolytic dissociation must disturb the constancy of the partition coefficients. Thus, if binary electrolytes are dealt with, and $\gamma$ is the dissociation coefficient of the saturated solution, then $c_1(1-\gamma)/x_1$, which refers only to the undissociated part, $\delta$, of the electrolyte, is constant; as, however, the author has previously pointed out (Abstr., 1896, ii, 160), Nernst's principle, according to which the dissociation coefficients of two electrolytes in a common solution are equal, and equal to the dissociation coefficient referred to the total concentration, is sometimes applicable. If the total molecular concentration remains constant, so does the dissociation, and consequently $c_1/x_1$ remains as constant as $c_1(1-\gamma)/x_1$; but if the total concentration changes, the relation $c(1-\gamma)=\kappa c^2\gamma^2$ holds, where $\kappa$ is the general equilibrium constant and $c$ is the volume concentration. It results from this that the dissociation coefficient in general decreases with increasing concentration, and *vice versâ*. The above relations must hold if only the undissociated material in solution determines the saturation equilibrium, but whether this is a permissible assumption has not previously been decided; Noyes (Abstr., 1893, ii, 565) considers it probable that both the dissociated and undissociated substance in solution determine its saturation. If this is the case, then neither $c_1(1-\gamma)/x_1$ nor $c_1\gamma/\sqrt{x}$ is constant, but their sum, namely,

$$c_1[1+\gamma(\sqrt{x}-1)]/x_1.$$

The influence of temperature changes on the relations indicated above is also considered. It is pointed out that, since double salts are dissociated into their component salts in solution, and Avogadro's principle does not apply to the crystalline state, there is, up to the present, no evidence that double salts are molecular complexes having the molecular composition usually stated.

The author has examined a number of cases of equilibrium between solid and liquid solutions of pairs of isomorphous salts. The equilibrium was established by three methods (1) By spontaneous evaporation of the aqueous solution of the two salts until mixed crystals separate at a temperature constant within 2° or 3°; (2) by evaporating the mixed solution, keeping the temperature at 30° by an Ostwald thermostat, and (3) by adding the salt $B$ to a solution of $A$ saturated at 25°, dissolving by heat, cooling again to 25°, and separating the deposited mixed crystals. The solid solutions, after powdering, were shaken at 25° with the corresponding liquid solution for some hours in order to ensure complete equilibrium.

The following pairs of salts were examined thus :—(4) potassium and ammonium chlorides, (4) potassium and ammonium bromides, (2) potassium bromide and chloride, (4) potassium and thallium nitrates, (1) barium and lead nitrates, (1) potassium and ammonium sulphates, (1) potassium sulphate and chromate, (1) lead and barium formates, (4) copper and nickel sulphates, (1) lead and strontium hyposulphates, (1) potassium copper sulphate and ammonium copper sulphate, (2) copper ammonium sulphate

and nickel ammonium sulphate, (1) or (2) copper ammonium sulphate and zinc ammonium sulphate, and (1) potassium and thallium alums. The number prefixed to each case refers to its place in Roozeboom's scheme of classification (Abstr., 1892, 265) of equilibria between solid and liquid solutions. The salt-pairs, potassium bromide and iodide, and potassium chloride and iodide, were examined, but the results were inconclusive; the behaviour of carbamide and thiocarbamide showed these substances to be not isomorphous. The mixed solution of the rhombohedral double salts, $CdCl_2,4KCl$ and $CdCl_2,4NH_4Cl$, on evaporation, deposit crystals of a typically different double salt. Experiments on mandelic acid and its salts also led to no satisfactory results.

The quantitative results show clearly that the expression

$$c[1 + \gamma(\sqrt{x} - 1)]/x$$

is much more nearly constant in most cases than either $c(1 - \gamma)/x$ or $c\gamma / \sqrt{x}$, thus demonstrating that the saturation of a liquid solution of an electrolyte is conditioned neither by the dissociated nor by the undissociated portion of the electrolyte alone; both the dissociated and undissociated part together determine the saturation of the solution.

The authors results further show that Nernst's solubility law, which states that the solubility of a salt decreases, if to its solution is added another salt having an ion in common with it, is erroneous; the exceptions to Nernst's law previously recorded have been attributed to the formation of molecular aggregates, but this the author shows to be untenable. It follows from this that Noyes' method of determining dissociation constants is not valid, although in many cases it may give approximately correct results. In place of Nernst's law, that the molecular concentration of the undissociated substance is a constant in mixed solutions, must be accepted the law that the sum of the concentration of the undissociated molecules and of the square of the concentration of the ions is a constant; this of course premises that no, or appreciably no, dissociation occurs in the solid solution. The new law is expressed by saying that $c[1 + \gamma(\sqrt{x} - 1)]$ is a constant for binary electrolytes; the relation is naturally more complex for ternary electrolytes. The principle holds that the solubility, or the equilibrium between several phases of variable composition, is governed by the law of chemical mass-action.

The conclusion clearly indicated by the author's work, namely, that the molecular weight in the crystalline state is identical with that of the chemical molecule, is of great crystallographic importance; it shows that Bravais' theory, that the molecules in a crystalline structure are disposed in parallel positions, is untrue, and consequently supports the later theory of Sohncke and Fedorow, which states that, in a crystalline structure, the arrangements of molecules is identical around each molecule.

Further, it is concluded that double salts and some salts containing water of crystallisation have not the molecular composition usually attributed to them; the constant proportion in which the various components of the solid salt separate together in the solid state is merely a result of the regular fitting together of those components in the crystal structure.

W. J. P.

**Permeation of Hot Platinum by Gases.** By WYATT W. RANDALL (*Amer. Chem. J.*, 1897, **19**, 682—691. Compare Ramsay and Travers, *Chem. News*, 1897, **75**, 253).—A platinum tube closed at one end, about 35 cm. long and 3 mm. internal diameter, was connected by the open end to a mercury pump and vacuum-tube (the latter for spectroscopic observations), whilst the other end, to the extent of $\frac{2}{3}$ to $\frac{3}{4}$ of the length of the tube, was inserted into a piece of hard glass tubing which was heated to a white heat; a dry gas was passed through the space between the two tubes, and the nature of any gas that diffused through the hot platinum into the vacuum of the pump was examined spectroscopically. Hydrogen was found to permeate the hot platinum, but much less slowly than Graham's statements lead one to expect; neither of the constituents of air will permeate it, nor will methane, in spite of its low density. Hydrogen, purified by filtration in this way, still exhibits the "compound" spectrum. C. F. B.

**Diffusion Constants of some Metals in Mercury.** By GEORG MEYER (*Ann. Phys. Chem.*, 1897, [ii], **61**, 225—234. Compare Humphreys, Trans., 1896, 243).—Des Coudres has measured the rate of diffusion of zinc in mercury by charging the surface of the mercury electrolytically with zinc, and measuring the potential difference between the surface and a zinc electrode, as the zinc gradually diffuses through the mass of the mercury. By a modification of this process, the author has determined the rates of diffusion of zinc, lead, and copper in mercury. The results are given in the following table:—

| | $k\ \frac{\text{cm.}^2}{\text{day}}$. | $t$. | K kg. | $l$ mm. | $u\ \frac{\text{mm.}}{\text{sec.}}$ |
|---|---|---|---|---|---|
| Zn ........... | 2·09 | 15·0° | $1·00 \times 10^9$ | $0·231 \times 10^{-8}$ | 332·2 |
| Cd .. ........ | 1·56 | 15·0 | $1·35 \times 10^9$ | $0·266 \times 10^{-8}$ | 253·1 |
| Pb ........... | 1·37 | 15·6 | $1·61 \times 10^9$ | $0·270 \times 10^{-8}$ | 186·4 |
| Au ...... ..... | 0·72 | 11·0 | $2·88 \times 10^9$ | $0·137 \times 10^{-8}$ | 189·3 |

$k$ is here the diffusion constant, and $t$ the temperature, K is the force required to move the gram-atom with the velocity 1 cm./sec. through the mercury, $l$ is the mean length of path, and $u$ the mean velocity of the atoms. The data for gold are those of Roberts-Austen, and are inserted for the purpose of comparison. H. C.

**Unit of Atomic Weights.** By FRIEDRICH WILHELM KÜSTER (*Zeit. anorg. Chem.*, 1897, **14**, 251—255).—A protest against Seubert's proposal to retain hydrogen as the unit of atomic weights, making O = 15·88 (this vol., ii, 137), in place of accepting O = 16 as the standard value. H. C.

**Basis of Atomic Weights.** By BOHUSLAV BRAUNER (*Zeit. anorg. Chem.*, 1897, **14**, 256—262).—The author recapitulates the many advantages of accepting O = 16 as the basis of atomic weights, and opposes Seubert's proposal to adopt the system H = 1 and O = 15·88 (compare preceding abstract). H. C.

**Determination of the Atomic Masses of Silver, Mercury, and Cadmium by the Electrolytic Method.** By WILLETT LEPLEY HARDIN (*J. Amer. Chem. Soc.*, 1896, 18, 990—1026).—Silver was deposited electrolytically from the nitrate, the acetate and the benzoate; the succinate was found to be unsuitable for the purpose. Ten observations were made in each case, and from the three series the final result Ag = 107·9275 was obtained (O = 16).

Mercury was deposited electrolytically from mercuric chloride, bromide, and cyanide, and, in addition, the ratio of the atomic mass of mercury to that of silver was determined by passing the same current through solutions of the two metals, and weighing the two deposits produced. The final result was Hg = 199·985 (O = 16).

Cadmium was deposited from the chloride and the bromide, the final result being Cd = 112·046 (O = 16). H. C.

**Equilibrium in Systems of Three Bodies, with Two Liquid Phases.** By FRANS A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1897, 23, 649—666).—The general case of the equilibrium between three liquids is first considered and a general form of the binodal curve is given. As an example of three-liquid equilibrium, the case of water, chloroform, and ethylic alcohol at 20° is considered, and the diagram given shows the quantity of chloroform necessary to cause the separation of aqueous alcohol into two layers, and the ratio of alcohol/water above which the liquid always remains homogeneous. Draper's and Schuncke's experiments (Abstr., 1894, ii, 378) on the solubility of ethylic ether in aqueous hydrochloric acid supply some data for the construction of the binodal curve for the equilibrium of the system ethylic ether, water, hydrogen chloride. When one of the compounds is a solid, the form of the curve is different, and consists of a number of portions from which are derived the limits of composition necessary for separation into (1) solid and two liquid layers; (2) two liquid layers; (3) solid and one liquid; (4) homogeneous liquid. This case is exemplified by the equilibrium of ammonium sulphate, water, and ethylic alcohol, the theoretical deductions being in accord with the experimental results of Bodländer. Other solids besides ammonium sulphate cause aqueous alcohol to separate into two layers, such as sodium and potassium hydoxides, sodium phosphate, potassium and sodium carbonates, &c. Lescoeur considered one of the layers formed on adding potassium carbonate to aqueous alcohol to be a definite hydrate of the composition $(C_2H_6O)_2,H_2O$, due, the author points out, to the temperature not being varied during the experiments. De Forcrand found (Abstr., 1883, 961) that in the system chloroform, water, hydrogen sulphide, a solid phase occurs corresponding with the composition $CHCl_3,2H_2S,23H_2O$; moreover, at low temperatures, the vapour phase possessed a constant composition independent of the quantity of the liquid phases, a result which must hold at constant temperature for a phase of a system in equilibrium.

L. M. J.

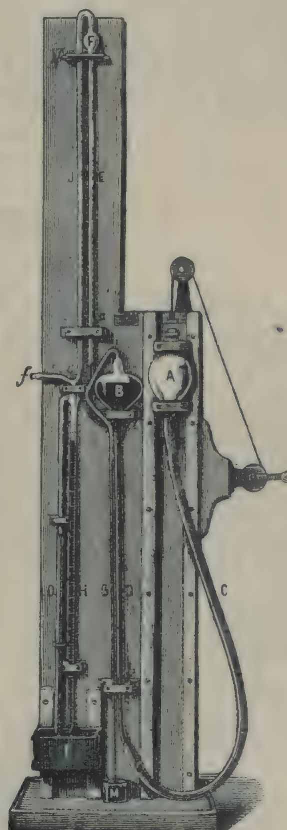
**Equilibrium in the System; Water, Sodium Chloride, and Ethylene Cyanide.** By FRANS A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1897, 23, 416—441).—The equilibrium in the system water,

and sodium chloride being known, that of water and ethylenic cyanide was first investigated, and the results are given in tabular form and as a curve. From these, it is seen that above 18·5° equilibrium exists between two liquid phases, that is, solution of the cyanide in water and of water in the cyanide, the critical point being 55°. At 42°, the densities of these two solutions are equal, so that the case exists of two liquids of equal density containing the same components but being non-miscible. At a higher percentage of cyanide, equilibrium between the pure compound and a solution of water in the cyanide is reached, so that at temperatures between 18·5° and 55° the addition of the cyanide gives the following states :—Solution of the cyanide in water, separation into two solutions, homogeneous liquid, separation into ethylenic cyanide and a solution of water in the cyanide. By the addition of salt, the region of equilibrium between the two solutions is extended, the critical point being 145°, the solution containing most cyanide being that with least salt. At the temperature 29°, a quintuple point exists where the phases, ethylenic cyanide, sodium chloride, solution 1, and solution 2 are in equilibrium. The various cases of equilibrium are fully discussed in the paper and illustrated by numerous diagrams. L. M. J.

**Application of the Phase-Law to Researches on Organic Additive Products.** By Basil B. Kuriloff (*Zeit. physikal. Chem.*, 1897, **23**, 673—685).—The author first investigated the solubility relations of $\beta$-naphthol and picric acid in a manner identical with that employed for the researches on triphenylmethane and benzene (this vol., i, 573). The curve again exhibits the three branches, namely, where the solid phase is (1) picric acid (2) the compound $C_6H_5(NO_2)_3{\cdot}OH,C_{10}H_7{\cdot}OH$, (3) $\beta$-naphthol, and with two quadruple points where the curves 1, 2, and 2, 3 cut one another. A maximum of temperature, 157°, occurs at the point where the composition represented is that of the compound, the curve on each side of this point giving the lowering of the melting point of the compound by addition of (1) $\beta$-naphthol, (2) picric acid, so that the cryoscopic relations are entirely in accord with the existence of the compound of melting point 157°. In the case of picric acid and benzene, however, although the curve still consists of the three portions corresponding with the three solid phases, there is no maximum, but at the point where the composition represented is that of the compound, the curve changes in direction and becomes that representing the lowering of the freezing point of the picric acid, that is, the melting point of the compound is also the quadruple point. Observations of the boiling point of solutions of $\beta$-naphthol in benzene gave a normal molecular weight, so that the tendency to form a compound is not apparent in boiling point observations. In the case of mixtures of benzene and $\beta$-naphthol, no compound is formed, the curve consisting solely of the two parts, namely, where the solid phase is (1) $\beta$-naphthol, (2) benzene. L. M. J.

**Explanation of the Deviations from the Normal Course of Reaction in the Case of Solutions.** By Ernst Cohen (*Zeit. physikal. Chem.*, 1897, **23**, 442—448).—The inversion of cane-sugar by acids does not follow the normal course of a monomolecular reaction, but

the velocity constant is greater at high than at low concentrations. Thus, at 25°, with N/2 hydrochloric acid, the values are, 40 per cent. – 29·16, 20 per cent. – 22·87, 10 per cent. – 20·63, 4 per cent. – 19·15. The author considers that these deviations are due to the same cause as deviations from Boyle's law, that is, to the volume of the sugar molecules, which, if not allowed for, would have the effect of increasing the constant at high concentrations. If the acid remain the same, and $b_{40}$ and $b_{20}$ be the percentage volumes of the sugar in the 40 and 20 per cent. solutions, then $k_{40}/k_{20} = (100 - b_{20})/(100 - b_{40})$ from which, assuming $b_{40} = 2b_{20}$, and using the above values of $k$, the result $b_{20} = 17·7$ is obtained. From this, the values $b_{10}$ and $b_4$ are calculated, and give the ratio $k_{10}/k_4 = 1·058$, that found experimentally being 1·077. Further researches to test the validity of the explanation were made with 30 per cent. and 15 per cent. solutions, which gave the value $b_{15} = 13·27$ leading to the same value as before for $b_{20}$. From the expression $k_p/k_q = c_p(100 - b_q)/c_q(100 - b_p)$ where $c_p$ and $c_q$ are the acid concentrations, the author deduces that a 12·5 per cent. solution should be inverted by N/16 hydrochloric acid at the same rate as a 25 per cent. solution by (N/16 ÷ 1·14) acid. The experimental results were in complete accord with theory, the rotation of the second solution remaining throughout double that of the first. From the values of $b_{20}$ and $b_{10}$, the ratio $k_{20}/k_{10}$ should be 1·10, and this was tested by the inversion with acids of various strengths, the ratio of the constants obtained being respectively 1·12, 1·11, 1·10, 1·10, 1·10; this is in complete accord with the theory. L. M. J.




**Mercury Pump without Stopcocks or Movable Joints.** By H. Henriet (*Compt. rend.*, 1897, **125**, 22—23) and Chabaud, *ibid.*, 107).—In this pump, valves and stopcocks are replaced by columns of mercury, and arrangements are made so that the first part of the exhaustion can be effected with a water pump. It will be readily understood from the illustration. The reservoir B terminates below in a vertical tube D which is connected with movable reservoir A. From the upper part of the tube D, just below its junction with B, there issues horizontally the tube E which is bent at right angles so that it is vertical, and returns on itself J, and terminates in a manometer tube H, at the junction with which

the tube *f*, for connecting with the vessel to be exhausted, issues horizontally. The upper part of the tube O, parallel with the manometer, is of glass, but the lower part is of caoutchouc for making connection with the water pump; when the water pump is disconnected, the caoutchouc tube is placed under the mercury in the same trough as the manometer. When A is lowered, the mercury runs out of B, and air enters at *f* and travels along J and E into B; when A is raised, the mercury rises in E and cuts it off, whilst the air in B is expelled through G and escapes through the small trough M.

Chabaud states that pumps constructed on similar principles have been in use in several laboratories for some time. C. H. B.

**A New Bottle for Washing Gases.** By Johann Walter (*J. pr. Chem.*, **55**, 507—508).—In this apparatus, the gas to be washed first passes down a vertical tube in the usual way; the bubbles issuing from it then separately enter the lower end of a worm surrounding the vertical tube of the bottle. In this way, the gas rises slowly through the worm in separate bubbles, and is thoroughly washed.

J. F. T.

## Inorganic Chemistry.

**Action of Light on Mixtures of Chlorine and Hydrogen.** By E. J. Armand Gautier and H. Hélier (*Compt. rend.*, 1897, **124**, 1267—1273; by Marcellin P. E. Berthelot, *ibid.*, 1273—1276, and by Armand Gautier, *ibid.*, 1276—1278).—When carefully dried hydrogen and chlorine in approximately equal volumes are exposed to diffused daylight (November) for a day, the proportion of hydrogen chloride formed is only about 2·55 per cent. of the mixture, whilst with the moist gases under similar conditions the quantity of hydrogen chloride may be as much as 60 per cent. When exposed for an hour to somewhat diffused autumn sunlight, the percentage of combination was 6·7 in the dry gases and 92·5 in the moist gases. It is clear, therefore, that the presence of water greatly accelerates the combination, a result probably due to the formation of intermediate products such as hypochlorous acid.

When the dry gaseous mixture was exposed at a distance of a metre to albo-carbon lights equivalent to 14·5 carcels, the percentage of combination was 92·5 after 237 hours. The rate of formation of hydrogen chloride at first increased until it reached a maximum of 2·8 per cent. per hour after 3 hours' exposure, and then it somewhat rapidly decreased, but neither in these cases nor in other exposures made to autumn sunlight was there any indication of a limit to the combination, and in this respect the action of light differs markedly from that of heat. With sunlight, the maximum rate of formation of hydrogen chloride is reached much more rapidly than with artificial light.

After the maximum has been passed, the rate of formation is not proportional to the number of uncombined hydrogen and chlorine atoms left in the mixture, because the hydrogen chloride already formed exercises a distinct retarding influence, although it does not limit the action.

In presence of an excess of chlorine, combination takes place more rapidly. With a mixture of Cl, 54·8 vols., H, 42·8 vols., and air 2·6 vols., combination was complete after 31 hours' exposure to the albo-carbon light, whilst with equal volumes of hydrogen and chlorine under similar conditions more than 250 hours were required. Excess of hydrogen has a similar, but less strongly marked, effect (compare this vol., ii, 437).

BERTHELOT considers that, in all investigations on the combination of mixed gases, it is essential to take into account possible reactions between the gases or the products of their combination and the material of the walls of the containing vessel (for example, the action of water on glass). In some cases, the combination of the gases and the action on the walls of the vessel may be simultaneous and not successive, the occurrence of any change at all being determined by the simultaneous action of chemical stresses between the gases and the material of the walls, which together constitute a heterogeneous system. Such local action on the walls will give rise to local thermal disturbances, and these may alter the nature or rate of the change in those regions. They may also lower the initial temperature at which changes will take place. Further, the reaction may be affected by the condensation of a film of gas on the surface of the containing walls. It is, in fact, the action of surfaces rather than the action of masses that has to be considered, and it is the surface actions that determine the equilibrium of the system.

GAUTIER replies that Berthelot's observations refer to his earlier experiments on the combination of gases when heated rather than to the present paper on the action of light on gases. He considers that the function of the walls of the vessel, which, in his experiments, were kept at a constant temperature and were not allowed to become heated by the combination, is to regulate the velocity of combination, and not to limit it. The phenomena with carbonic oxide and oxygen are similar to those with hydrogen and oxygen, but in the former case it is impossible to assume the formation of hydrates. Moreover, the results are the same with vessels of glass, silvered glass, porcelain, or quartz, and are not affected by different methods of cleaning and washing the internal surfaces. C. H. B.

**Rendering Oxygen Active during the Slow Oxidation of Sodium Sulphite.** By W. P. JORISSEN (*Zeit. physikal. Chem.*, 1897, 23, 667—672).—The increased activity of oxygen during the oxidation of sulphurous acid or metallic sulphites had been previously observed by Mohr, Liebig, and Wicke. The author, therefore, endeavoured to ascertain whether in this case, as in those previously determined (this vol., ii., 253), the quantity of oxygen rendered active is equal to that used for the oxidation. Preliminary experiments showed that, during the oxidation of sodium sulphite by exposure to air, the quantity of

oxygen used is precisely that necessary for the conversion of the sulphite into sulphate. A solution of sodium sulphite, potassium hydrogen carbonate, and arsenic trioxide was next exposed to air, and it was found, in accordance with Mohr's experiments, that, in this case, the arsenic trioxide also oxidises, and that if a sufficient quantity of the carbonate is employed, the total quantity of oxygen used is double that required by the sulphite alone, and is independent of the quantity of the trioxide, so that here also the oxygen rendered active is equal in amount to that required by the sulphite itself. The author does not consider that the known facts justify the conclusions of Ihle and Bach regarding the cause of this increased activity. (Compare this vol., ii, 401, 402). L. M. J.

**Tables of the Specific Weight of Solutions of Sulphur in Carbon Bisulphide.** By GEORGE J. PFEIFFER (*Zeit. anorg. Chem.*, 1897, **15**, 194—203).—A Sprengel-Ostwald's pyknometer was employed in the determinations, and in order to prevent the evaporation of the bisulphide, the capillary tube of the pyknometer was closed with a drop of water when full to the mark with the solution at 15°. It was then placed in ice-cold alcohol, and the drop of water absorbed by filter paper. After the solution had contracted, the apparatus was washed with cold ether, dried, and weighed. The results are tabulated. E. C. R.

**Action of Telluric Chloride and Fluoride on the Corresponding Hydracids.** By RENÉ METZNER (*Compt. rend.*, 1897, **125**, 23—26).—When hydrogen chloride is passed into a solution of tellurium chloride in a concentrated solution of hydrochloric acid at $-23°$, no precipitate forms, but if the liquid is cooled to $-30°$, the compound $TeCl_4,HCl + 5H_2O$ separates in slender, lemon-yellow needles, resembling the hydrobromide of the bromide (following abstract). It readily decomposes, with loss of hydrogen chloride.

When tellurous anhydride is dissolved in concentrated hydrofluoric acid, the liquid concentrated, the crystalline residue dissolved in hydrofluoric acid, and the liquid saturated with hydrogen fluoride at $-20°$, the compound $2TeF_4,3TeO_2 + 6H_2O$ separates in long, transparent crystals. When heated in hydrogen, they decompose, all the tellurium being converted into tellurous anhydride, and all the fluorine into hydrogen fluoride.

When the mother liquor from the preceding compound is more strongly cooled, with frequent stirring, the walls of the vessel being rubbed, the compound $TeF_4,TeO_2 + 2H_2O$ separates in large needles; like the preceding compound, it is decomposed by water. When heated, it yields tellurous anhydride and hydrogen fluoride.

The method adopted for analysing both these oxyfluorides is described in detail.

Telluric fluoride crystallises from its solution when the latter is saturated with hydrogen fluoride at $-50°$ and is cooled for a short time to $-70°$; the crystals, when once formed, melt very slowly, even at $-23°$. The formation of a hydrofluoride of the fluoride seems to require a very low temperature. C. H. B.

**Combination of Telluric Bromide and Iodide with the Corresponding Hydracids.** By René Metzner (*Compt. rend.*, 1897, **124**, 1448—1451).—If tellurous anhydride is dissolved in a cold saturated solution of hydriodic acid, and hydrogen iodide passed into the liquid, heat is developed, and black, quadratic needles with a metallic lustre separate, the yield being much greater if the liquid is cooled so that a large quantity of hydrogen iodide is dissolved. The crystals have the composition $TeI_4,HI + 8H_2O$; they do not fume in the air, but are deliquescent, changing rapidly to a deep brown, viscous liquid. When heated out of contact with air, they melt constantly at 55°, and at a higher temperature, lose water and hydrogen iodide, a grey metallic-looking residue of telluric iodide being left. This iodide, when heated in the air, decomposes with incandescence, iodine being liberated, and tellurous anhydride formed.

The bromine compound is obtained in a similar manner, the liquid preferably being cooled to −15°. It forms slender, red, prismatic needles of the composition $TeBr_4,HBr + 5H_2O$. They remain unchanged for a long time in an atmosphere of hydrogen bromide, melt at 20° with liberation of hydrogen bromide, and fume and deliquesce in moist air. C. H. B.

**Phosphorus Iodides.** By J. Adolphe Besson (*Compt. rend.*, 1897, **124**, 1346—1349).—Phosphorus tri-iodide is best prepared by the action of dry hydrogen iodide on phosphorus trichloride either alone or in presence of carbon tetrachloride. It melts at 61°, and is completely decomposed by water without liberation of iodine or formation of any insoluble product. Under a pressure of 15 mm., it begins to sublime below 100°, and sublimation becomes active at 120°, but if this temperature is exceeded, there is danger of decomposition. When dissolved in carbon bisulphide, the tri-iodide is reduced by mercury, the first product being the iodide $P_2I_4$, but with excess of mercury the ultimate products are mercurous iodide and a double mercury phosphorus iodide; this reaction is useful for the removal of the tri-iodide from mixed solutions. Silver behaves similarly, but the reduction stops at the di-iodide.

Phosphorus di-iodide melts and slightly decomposes at 110°. Under a pressure of 15 mm., even below 100°, it gives a sublimate of the tri-iodide, and the decomposition is more rapid at 120°, a residue of amorphous phosphorus being left. When treated with mercurous chloride, the di-iodide yields phosphorus trichloride, mercurous iodide, and phosphorus, the latter being entirely insoluble in carbon bisulphide. It is probable that in Gautier's reaction of the di-iodide with silver chloride, the phosphorus is likewise liberated in the amorphous form.

When a solution of iodine in carbon tetrachloride is added to carbon tetrachloride at the bottom of which there is a layer of fused phosphorus, the iodine is converted into phosphorus di-iodide, which remains in solution, and the phosphorus becomes covered with a layer of amorphous phosphorus. Some phosphorus is, of course, also dissolved by the tetrachloride, and the solution seems to contain an unstable compound, $P_3I_4$, which is decomposed by light, heat, or the concentration of the solution yielding amorphous phosphorus and the di-iodide,

which is again converted into the unstable compound, this cycle of changes constituting the mechanism by which white phosphorus is converted into the amorphous form. C. H. B.

**Calcium Fluoride in a Fossil Elephant's Bone from the Tertiary.** By JACOBUS M. VAN BEMMELEN, A. SIMON-THOMAS, and EDUARD A. KLOBBIE (*Zeit. anorg. Chem.*, 1897, 15, 84—89).—The research was undertaken in order to determine if the bones from the strata in which Dr. E. Dubois discovered the remains of *Pithekanthropos erectus* contain fluorine and phosphoric acid in the ratio which has been determined by Carnot for Pliocene remains. The ratio for the air-dried substance was found to be 0·0478, for apatite it is 0·0892 : $\frac{0\cdot0478}{0\cdot0892} = 0\cdot53$. Carnot, for bones from the Pliocene, gives the ratio 0·58. The authors point out that too much dependence must not be placed on these ratios, as the absorption of fluorine is not only dependent on the time (age of the strata), but also on the nature of the strata and the composition of the water flowing through the strata. E. C. R.

**Absorption of Calcium Fluoride, Lime, and Phosphates in Fossil Bones.** By JACOBUS M. VAN BEMMELEN and EDUARD A. KLOBBIE (*Zeit. anorg. Chem.*, 1897, 15, 90—122).—The microscopical examination of a tibia of a fossil Stegodon shows that the outside is composed of a hard crust of calcium carbonate. In the compact portion, the Hafer's canals are filled with white, crystalline calcium carbonate, whilst in the outside portion many of the canals are filled with pyrites; the inner portion of the compact part is bright brownish-yellow and free, or almost free, from pyrites. In the spongy portion, pyrites is also present, and the holes are entirely filled with calcium carbonate sometimes containing pyrites. In the axial hole of the spongy portion, the structure is almost entirely destroyed, and the sides of the hole covered with large crystals of calcium carbonate. The compact portion gave, on analysis, 30·3 $P_2O_5$, 1·45 F, 6·11 $CO_2$, 0·1 $K_2O$, 49·14 CaO, 0·31 MgO, 1·28 MnO, 0·61 $Fe_2O_3$, 0·41 $FeS_2$, 0·05 insoluble, 2·2 organic substance, 4·21 $H_2O$ at 110° and 4 per cent. $H_2O$ at a higher temperature. A sample containing some of the spongy portion gave 27·77 $P_2O_5$, 1·33 F, 8·61 $CO_2$, 0·06 $K_2O$, 48·08 CaO, 0·3 MgO, 1·25 MnO, 0·65 $Fe_2O_3$, 2·55 $FeS_2$, 0·35 insoluble, 1·7 organic substance, 3·7 $H_2O$ at 110° and 4 per cent. of water at a higher temperature. The compact portion has the sp. gr. = 2·2. The structure of the bone is not altered. A consideration of the above analyses taken in conjunction with the high specific gravity and the fact that the structure of the bone is unaltered, points to the conclusion that there has been an absorption from the water of the strata, not only of calcium carbonate, but also of calcium phosphate into the compact portion. A portion of the calcium carbonate is converted into calcium fluoride (3 per cent.), also about half the magnesium phosphate and a small portion of the calcium phosphate is converted into manganese and ferric phosphates. The phosphate, by the absorption of lime, has become basic to such an extent that one-eighth more base is present than is required for the ratio 2 mols. orthophosphate to 1 mol. base. The absorption of these compounds is due to

the original phosphate in the bone; they do not form a chemical compound, but a hydrated absorption complex. E. C. R.

**Action of Zinc on Hydrogen Chloride Dissolved in Organic Solvents.** By F. Zecchini (*Gazzetta*, 1897, 27, i, 466—473).—The author has examined the action of zinc on solutions of hydrogen chloride of known concentration in methylic, ethylic, and amylic alcohols and in acetone and ethylic ether; the zinc was allowed to act for a known length of time and the amount of hydrogen chloride decomposed determined by titration with standard potash. The zinc used was in the form of cylinders exposing 278 sq. mm. of surface and the solution was kept agitated and at the constant temperature of 20° during the experiment; the organic solvents used were carefully dehydrated, and the solutions being of one-half or one-third normal concentration in hydrogen chloride. The anhydrous solutions of hydrogen chloride in methylic alcohol, ethylic alcohol, and acetone in all cases acted rapidly on the zinc, and in some cases more rapidly than did an aqueous solution of hydrogen chloride of the same concentration; the addition of small quantities of water to the organic solutions of hydrogen chloride causes them to act less rapidly on the zinc. Dry amylic alcohol solutions of hydrogen chloride act very slowly on the metal.

The dry ethylic ether solutions of hydrogen chloride act far more rapidly on zinc than do aqueous solutions of the same concentration, and the addition of about 0·5 per cent. of water causes the action to proceed some four times as rapidly as before. This behaviour of ethereal solutions of hydrogen chloride is very remarkable in connection with the electrolytic dissociation hypothesis according to which the reactivity of an acid is measured by its dissociation. Hydrogen chloride is not dissociated in ethereal solution, yet it acts much more rapidly on zinc in ethereal than in aqueous solutions of the same concentration.

W. J. P.

**Basic Cupric Salts and Brown Cupric Hydroxide.** By Paul Sabatier (*Compt. rend.*, 1897, **125**, 101—104).—The author uses the term *principal basic salts* to denote those salts which are formed by the direct action of the oxide or hydroxide on solutions of the normal salt. The principal basic salts of copper are of the type $CuR_2,3CuO + 3H_2O$, except that the sulphate contains $4H_2O$. The acetate is an exception and is of the type $CuR_2,2CuO + 2H_2O$.

All these salts except the acetate contain the bivalent group $Cu_4O_3$, and it appears probable that the same group is present in the brown hydroxide formed by the spontaneous dehydration of the blue hydroxide. This brown product has the composition $Cu(OH)_2,3CuO$, or $Cu_4O_3(OH)_2$. As a matter of fact, this brown hydroxide readily forms the principal basic salts when placed in contact with solutions of normal cupric salts. The basic nitrate thus obtained is crystallised in minute rhombic or hexagonal lamellæ derived from a monoclinic prism; when left in contact with the nitrate solution, the lamellæ change into needles. The blue hydroxide yields the same basic salt, but in an amorphous form. The basic chloride formed under similar conditions is amorphous; the basic bromide forms small, deep green, hexagonal lamellæ; the basic sulphate forms small, elongated prisms; the basic

dithionate crystallises in small, hexagonal lamellæ, and the basic chlorate in microscopic rhombic plates.

Solutions of the acetate and of the perchlorate, on the other hand, have no action on the brown hydroxide. C. H. B.

**Action of Ammonia on Mercurous Iodide.** By MAURICE FRANÇOIS (*J. Pharm.*, 1897, [vi], **5**, 388—392).—Ammonia acts on mercurous iodide in the cold, yielding metallic mercury and ammoniacal mercuric iodide, $HgI_2,2NH_3$; the latter is colourless, and is only stable in the presence of an excess of ammonia. The reaction was followed quantitatively by extracting the products with ether, which dissolves out the ammoniacal mercuric iodide.

If a large excess of ammonia is used, dimercuryammonium iodide and tetramercuryammonium iodide are formed.

Mercurous chloride appears to react with ammonia in much the same manner, and it is probable that the grey product formed consists of a mixture of free mercury and of one of the already known compounds of mercuric chloride with ammonia. J. J. S.

**Atomic Weight of Cerium.** By GREGOIRE N. WYROUBOFF and AUGUSTE V. L. VERNEUIL (*Compt. rend.*, 1897, **124**, 1300—1303).—The only cerium compound available for accurate determinations of the atomic weight is cerium sulphate, $3CeSO_4 + 8H_2O$. The composition of the hydrated salt is very constant, and the atomic weight may be determined from the loss of water at about 250°, or the loss of sulphuric anhydride at a higher temperature, the ratio of the residual oxide, $Ce_3O_4$, being calculated to either the anhydrous or hydrated salt.

Cerium prepared in different ways from monazite and cerite, and purified in the manner previously described (this vol., ii, 452), has an atomic weight of 92·70 to 92·87 [Ten determinations; standard not stated], these figures being probably accurate to within 0·2 or 0·3 per cent. C. H. B.

**A Process of Oxidation and Chlorination [by Manganese Salts].** By ANTOINE VILLIERS (*Compt. rend.*, 1897, **124**, 1349—1351).—When a mixture of equal volumes of a saturated solution of oxalic acid, hydrochloric acid of 25 per cent., and nitric acid of 25 per cent. is heated, there is no evolution of gas, but if a small quantity of any manganese salt is added there is an almost immediate reaction with evolution of carbonic anhydride and nitrogen, and the decomposition proceeds even if heating is discontinued. If the nitric acid is in excess, the oxalic acid is completely oxidised. With more concentrated solutions, the oxalic acid is slightly decomposed even in absence of manganese, but the difference produced by the addition of manganese is very marked. Many other compounds of the fatty group, such as glucose and saccharose, behave in the same way. Compounds of the benzene group, on the other hand, yield chlorine substitution products instead of oxidation products; benzene and toluene, for example, yield chlorobenzene and chlorotoluene respectively, even at the ordinary temperature.

This property of transferring oxygen from one compound to another, possessed in so marked a degree by even small quantities of manganese,

is of special interest in connection with the co-existence of manganese and oxidising ferments in vegetables, as observed by Bertrand (following abstract). The decomposition of oxalic acid, in the manner described, has many points of resemblance to oxidations produced by oxidising ferments, and may perhaps be regarded as an example of "inorganic fermentation." C. H. B.

**Oxidising Action of Manganese Salts: Constitution of Oxydases.** By GABRIEL BERTRAND (*Compt. rend.*, 1897, **124**, 1355—1358).—All manganese salts have the property of bringing about the oxidation by atmospheric oxygen of solutions of quinol, pyrogallol, and paramidophenol, guaiacum, and similar substances. The solution acquires a colour which depends on the nature of the carbon compound, whilst the intensity of the coloration depends on the nature of the acid in combination with the manganese. Oxidation is much more energetic with salts such as the succinate, gluconate, or salicylate than with the chloride, sulphate, or nitrate.

Manganese salts in aqueous solution are partially hydrolysed, the degree of hydrolysis being greater with feeble organic acids than with inorganic acids. The manganous oxide oxidises in contact with air, and this change involves the splitting up of the molecules of atmospheric oxygen, one atom of the molecule combining with the manganous oxide, whilst the other atom is free to combine with any other oxidisable substance with which it may come in contact. The latter may, under these conditions, be oxidised, although it would resist the action of oxygen in the form of molecules. Quinol, when mixed with manganous oxide and agitated with air, is oxidised to quinone, and manganese peroxide is formed. In presence of acids, the manganese peroxide is converted into a manganous salt, a further quantity of the carbon compound being oxidised at the same time. If manganese peroxide is suspended in a dilute acid which has no action on it at the ordinary temperature, and quinol is added, then the manganese dissolves and quinone is formed.

These results, and those previously described, tend to the view that the oxydases are special compounds of manganese in which the acid radicle, of a proteid character and varying with the particular ferment, has just sufficient activity to keep the metal in solution, whilst the metal is the real carrier of oxygen. C. H. B.

**Function of Manganese in Certain Oxidations.** By ACH. LIVACHE (*Compt. rend.*, 1897, **124**, 1520—1521).—The author points out that the influence of manganese in promoting the oxidation of organic substances as described by Villiers and by Bertrand (preceding abstracts), is similar to the effect that he observed some years ago (Abstr., 1884, 532) in the case of drying oils, and the explanation is doubtless the same in all cases. C. H. B.

**Constitution of Inorganic Compounds. No. IX. Triammine and Diammine Cobaltic Salts.** BY ALFRED WERNER (*Zeit. anorg. Chem.*, 1897, **15**, 143—172).—The triammine salts are prepared from dichloroaquotriammine cobaltic chloride, which is separated from the small quantity of tetrammine salt, formed during its preparation, by

treating it with mercuric chloride, whereby the tetrammine salt is precipitated as an insoluble mercury double salt.

*Acid dichloraquotriamminecobalt sulphate*, $[Co(NH_3)_3H_2OCl_2]SO_4H$, is obtained by mixing the dichloraquotriammine chloride to a thin paste with a cooled mixture of concentrated sulphuric acid (2 vols.) and concentrated hydrochloric acid (1 vol.), and after the mixture has remained 1 hour, spreading the paste on a porous plate. This operation is repeated three times, and the product then washed with alcohol until free from acid, and dried over sulphuric acid. It is a greyish-green, crystalline powder, and dissolves fairly easily in water yielding a green solution which quickly changes to indigo blue; the solution has an acid reaction. It is obtained in black, lustrous, prismatic crystals by adding concentrated sulphuric acid to the cold concentrated aqueous solution and evaporating the clear liquid in a vacuum over sulphuric acid. The *silver* derivative is obtained by thoroughly mixing the acid sulphate with a small quantity of silver nitrate solution and washing the product with absolute alcohol. It is a grass green powder which quickly decomposes and darkens, and when treated with water decomposes with separation of silver chloride.

*Dichloraquotriamminecobalt nitrate*, $[Co(NH_3)_3H_2OCl_2]NO_3$, is obtained by treating the dichloro-chloride with concentrated nitric acid, and washing the greyish-green precipitate with alcohol and ether until free from acid. It dissolves in water, forming a green solution which quickly changes to blue.

*Bluish-grey chloraquotriamminecobalt sulphate*,

$$[Co(NH_3)_3(H_2O)_2Cl]SO_4,$$

is obtained by dissolving the above acid sulphate in water and precipitating the indigo-coloured solution with an equal volume of alcohol. It dissolves in water with an indigo-blue coloration, and, if kept, the solution deposits crystals of the sparingly soluble violet salt described below. When the solution is treated with hydrochloric acid, dichloraquotriamminecobalt chloride is obtained.

*Grey dichloraquotriamminecobalt chloride*, $[Co(NH_3)_3H_2OCl_2]Cl$, is obtained by treating the preceding salt with concentrated hydrochloric acid. It has the same percentage composition as the dichro-cobalt chloride, but is not identical with that salt. It dissolves in water, forming a pure blue solution which changes to violet, whereas the dichro-cobalt chloride yields a green solution which changes to blue and then violet. When treated with concentrated nitric acid, it yields a nitrate which gives a green solution gradually changing to blue, and then to violet. The nitrate obtained from the dichro-cobalt chloride also yields a green solution, but this changes to blue and violet more quickly than the preceding nitrate.

*Violet chlorodiaquotriamminecobalt sulphate*, $[Co(NH_3)_3(H_2O)_2Cl]SO_4$, is obtained by heating an aqueous solution of the acid sulphate on the water bath and allowing the solution to crystallise in a vacuum. It separates in small, lustrous crystals, is almost insoluble in water, and can also be obtained by treating the following salt with sulphuric acid.

*Chlorodiaquotriamminecobalt chloride*, $[Co(NH_3)_3(H_2O)_2Cl]Cl_2$, is obtained by treating the preceding salt with concentrated hydrochloric

acid. It is a dark-violet, crystalline powder, and dissolves in water to a pure violet solution. When treated with nitric acid, the corresponding *nitrate* is obtained as a bright violet, crystalline powder. When warmed with hydrochloric acid, dichloraquotriamminecobalt chloride is obtained.

*Sulphatodiaquotriamminecobalt sulphate*, $[Co(NH_3)_3(H_2O)_2SO_4]_2SO_4 + H_2O$, is obtained by adding the requisite quantity of silver sulphate to a warm, concentrated solution of dichloraquotriamminecobalt chloride, and evaporating the filtrate from the silver chloride in a vacuum. The residue is extracted with water, when the salt is left undissolved; by evaporating the solution and again extracting with water, a further quantity of the insoluble salt is obtained. It is a reddish-violet powder, insoluble in water, but soluble in concentrated hydrochloric, nitric, and sulphuric acids. When mixed with concentrated hydrochloric acid, it yields chlorodiaquotriammine sulphate, and by the prolonged action of the acid, the dichloraquocobalt chloride.

*Oxalodiaquotriamminecobalt nitrate*, $[Co(NH_3)_3(C_2O_4)(H_2O)_2]NO_3$, is obtained by treating dichloraquotriamminecobalt chloride with a cold saturated solution of oxalic acid, and, after adding an equal volume of alcohol, warming the mixture for one minute. On cooling, oxalochlorotriamminecobalt crystallises out. This is treated with the theoretical quantity of silver nitrate and the filtrate allowed to crystallise. It crystallises in silky, carmine-red crystals, and is sparingly soluble in cold water, easily so in warm water. When warmed for a short time with hydrochloric acid, it is converted into *chloroxaloaquotriamminecobalt*, $Co(NH_3)_3ClHO_2(C_2O_4)$, which is a violet powder, insoluble in water. When treated with a few drops of acetic acid and sodium nitrite, it yields *nitroxalotriamminecobalt*, $Co(NH_3)_3C_2O_4{\cdot}NO_2$, which is a cherry-red, crystalline powder insoluble in water.

*Derivatives of the diamminecobaltic series* are prepared from potassium tetranitritodiamminecobalt, which is prepared by Jörgensen's method (*J. pr. Chem.*, [ii], **23**, 249), somewhat modified, as follows: 500 c.c. of a neutral solution of cobalt carbonate (20 grams) in hydrochloric acid is treated with ammonium chloride (100 grams) and the mixture heated to 50°; a solution of pure potassium nitrite (250 grams) in water (250 c.c.), also heated to 50°, is then gradually added, and the mixture kept at 40—50°, for 20—30 minutes, and allowed to cool. After 24 hours, the prismatic crystals of the potassium salt are washed free from the fine, greenish-yellow precipitate, and recrystallised from water. It is most important that the potassium nitrite should be pure. If less potassium nitrite is employed, or the mixture heated for a longer time at 50—60°, a mixture of potassium tetranitritodiamminecobalt with trinitritotriamminecobalt is obtained.

*Acid dichlorodiaquodiamminecobalt sulphate*,

$$[Co(NH_3)_2(H_2O)_2Cl_2]SO_4H,$$

is obtained by adding the preceding potassium salt (3 grams) to a mixture of equal volumes of sulphuric and hydrochloric acids, cooled with ice and salt, and allowing the mixture to remain some hours in the freezing mixture. After 24 hours, the product is washed with alcohol and ether, dissolved in ice-cold water, and precipitated with sulphuric acid. It crystallises in lustrous, malachite-green needles, is easily

soluble in water, and yields a green solution which quickly changes to blue. The solution has an acid reaction.

*Dichlorodiaquodiamminecobalt nitrate*, $[Co(NH_3)_2(H_2O)_2Cl_2]NO_3$, is obtained by treating a cold solution of the preceding salt with concentrated nitric acid. It is a dark-green, crystalline powder, dissolves easily in water, forming a green solution which quickly becomes blue, and decomposes, when kept in a closed vessel, yielding an insoluble brown powder containing cobalt oxide. The *chloride*, $[Co(NH_3)_2(H_2O)_2Cl_2]Cl$, is obtained by treating the acid sulphate with hydrochloric acid. It is a malachite-green, crystalline powder easily soluble in water, yielding a green solution which changes to blue.

*Chlorotriaquodiamminecobalt sulphate*, $[Co(NH_3)_2(H_2O)_3Cl]SO_4 + H_2O$, is obtained by allowing a solution of the acid sulphate to remain at the ordinary temperature, and after adding a few drops of sulphuric acid, evaporating the solution in a vacuum over sulphuric acid. It separates in short, indigo-blue crystals, and is less soluble than the acid sulphate.

*Isomeric dichlorodiaquodiamminecobalt chloride*,

$$[Co(NH_3)_2(H_2O)_2Cl_2]Cl,$$

is obtained by treating the preceding salt with concentrated hydrochloric acid until all the sulphuric acid is eliminated. It is a green powder which dissolves easily in water when it at once gives a blue solution. E. C. R.

**Fluidity of Fused Nickel.** By JULES GARNIER (*Compt. rend.*, 1897, **124**, 1447—1448).—When fused at a high temperature, nickel is very mobile, and readily penetrates charcoal, forming, when cold, slender, hair-like filaments, very flexible and malleable. C. H. B.

**Reduction of Molybdic Anhydride by Hydrogen.** By M. GUICHARD (*Compt. rend.*, 1897, **125**, 26—29 and 105—106).—The statements of different chemists as to the products of the reduction of molybdic anhydride by hydrogen are very conflicting, and the author has therefore reinvestigated the reaction, special attention being directed to the possible production of oxides intermediate between the trioxide and the dioxide. The hydrogen was carefully purified and dried; the oxide was contained in a U-tube heated in a bath of melted tin. For temperatures above 500°, the oxide was placed in a dish in a straight tube surrounded by asbestos and placed in an iron gutter, the temperatures being measured by means of a thermoelectric couple.

Reduction begins at about 300°, the yellow colour changing to bluish-grey, but it is not rapid below 470°; the only product under these conditions is the dioxide $MO_2$, and examination of the residue at various stages of the reduction shows that no intermediate oxide is formed.

The dioxide begins to lose oxygen at about 500°, reduction becoming very distinct at 550°, and more rapid at 600°; the sole product is metallic molybdenum, the product of incomplete reduction at any stage being a mixture of the metal with the dioxide.

Contrary to the statement of Liechti and Kempe, molybdenum dioxide does not volatilise when heated in hydrogen chloride.

C. H. B.

**Salts of Sulphomolybdic Acid.** By ARTHUR ROSENHEIM (*Zeit. anorg. Chem.*, 1897, **15**, 180—191).—Since the author's previous communication (Abstr., 1895, ii, 18), Friedheim and Euler have published their iodometric method for the estimation of molybdic acid (Abstr., 1895, ii, 535), and on repeating the analyses of the salts previously described the author finds that his results were incorrect.

*Action of Sulphurous Acid on Paramolybdates.*—The sulphomolybdates are obtained by treating a saturated solution of the paramolybdate at the ordinary temperature with sulphurous anhydride; the potassium and sodium salts have been previously described. The cæsium and rubidium salts are very similar to the potassium salt, but the lithium salt could not be obtained pure, as it is more soluble than lithium sulphite, and on further concentration of the solution decomposition takes place. The salts have the following composition: $2Na_2O,2SO_2,5MO_3 + 8H_2O$; $2K_2O,2SO_2,5MO_3 + H_2O$; $2Rb_2O,2SO_2,5MO_3 + \frac{1}{2}H_2O$; $2Cs_2O,2SO_2,5MO_3 + 6H_2O$. They decompose if allowed to remain in the mother liquor for some time, the corresponding trimolybdate being precipitated; and, even when dry, they gradually decompose with evolution of sulphurous anhydride. When a dilute solution of ammonium paramolybdate is treated at the ordinary temperature with sulphurous anhydride, the salt $3(NH_4)_2O,2SO_2,8MO_3 + 5H_2O$ is formed; if, however, the solution is well cooled, a mixture of this salt with the *salt* $2(NH_4)_2O,2SO_2,5MO_3 + 12H_2O$ is obtained. The latter salt, which is obtained pure by adding a saturated solution of ammonium chloride to a freshly prepared concentrated solution of the sodium salt, crystallises in long, white needles, and very readily decomposes with evolution of sulphurous anhydride. Although the corresponding salts of the alkaline earths cannot be prepared by the action of sulphurous anhydride on the paramolybdates suspended in water, the *barium* and *strontium* salts are easily obtained by treating a freshly prepared solution of the sodium salt with the corresponding chlorides, and allowing the mixture to evaporate slowly over sulphuric acid; they crystallise in prismatic needles. The *calcium* salt, which crystallises in needles, cannot be obtained pure owing to its great solubility. Salts analogous to the stable ammonium salt, $3(NH_4)_2O,2SO_2,8MO_3 + 5H_2O$, cannot be prepared by double decomposition, for either the ammonium salt separates unchanged, or decomposition takes place with the formation of trimolybdates.

When normal molybdates, $R_2O,MO_3$, are treated with sulphurous anhydride in excess, the same salts are obtained as with the paramolybdates. If, however, the solution is not completely saturated with sulphurous anhydride, a mixture of sulphomolybdate and paramolybdate is obtained.

*Action of Sulphurous Acid on Tetramolybdates.*—When solutions of tetramolybdates, $R_2O,4MO_3$, are treated with sulphurous anhydride, octamolybdates, $R_2O,8MO_3$, are formed, but a sulphomolybdate could not be obtained. This is a very convenient method of preparing these salts. The potassium salt, $K_2O,8MO_3 + 13H_2O$, and the sodium salt, $Na_2O,8MO_3 + 15H_2O$, crystallise in well characterised prisms, the *ammonium* salt, with $13H_2O$ in lustrous, prismatic needles.

E. C. R.

**Manganimolybdates.** By E. Péchard (*Compt. rend.*, 1897, **125**, 29—31).—When a solution of ammonium hydrogen molybdate is boiled with manganese peroxide, the liquid acquires a ruby-red colour, and when cooled deposits crystals of a new complex salt. Manganese peroxide prepared in various ways gives the same result, but the reaction is slow. A better method is to precipitate ammonium manganous molybdate by mixing solutions of the molybdate and a manganous salt; suspend this in water and add gradually a dilute solution of potassium permanganate. Another plan is to mix hot solutions of the molybdate and potassium permanganate, and reduce the latter by adding alcohol, aldehyde, &c. In both cases, the permanganate may be replaced by permanganic acid.

The *manganimolybdates* thus formed are readily crystallisable, red salts of the composition $3M'_2O,MnO_2,12MO_3$. They are stable at the ordinary temperature, but, when heated, decompose into manganese peroxide and an acid molybdate. Their solutions yield a precipitate of the peroxide when mixed with an acid or an alkali.

The ammonium salt contains $5H_2O$, and forms small, deep-red crystals slightly soluble in water; the potassium salt crystallises with $4H_2O$, is paler in colour than the ammonium salt, and is almost insoluble in water; the sodium salt crystallises with $13H_2O$ in large, efflorescent, blood-red crystals very soluble in water. The free acid obtained by the action of sulphuric acid on the barium salt does not crystallise, but when evaporated to dryness in a vacuum, forms a brilliant, black, amorphous mass with a vitreous fracture; it has the composition $MnO_2,12MO_3 + 10H_2O$, and its properties are similar to those of its salts.

Tungstic acid seems to yield no analogous compounds.

C. H. B.

**Zirconotungstates.** By L. A. Hallopeau (*Bull. Soc. Chim.*, 1896, [iii], **15**, 917—923).—*Potassium zirconodecatungstate*, $4K_2O,ZrO_2,10WO_3 + 15H_2O$, is prepared by dissolving gelatinous zirconia in a solution of potassium paratungstate with prolonged boiling. After filtration and concentration of the solution in a vacuum, it is obtained as a crystalline powder having a slight action on polarised light. From the mother liquor, on further concentration in a vacuum, *potassium dizirconodecatungstate*, $4K_2O,2ZrO_2,10WO_3 + 20H_2O$, is deposited; this forms very small, prismatic crystals, which act more powerfully on polarised light than those of the preceding compound, and lose $12H_2O$ at 100°. These substances are very slightly soluble in cold, but much more readily in hot water. They decompose on ignition, giving insoluble products, and, when fused with alkali carbonates are converted into a mixture of tungstate and zirconate, with abundant disengagement of carbonic anhydride. When the dizirconodecatungstate is heated to dull redness with an excess of sodium carbonate, the following reaction occurs:

$$4K_2O,2ZrO_2,10WO_3,20H_2O + 8Na_2CO_3 = 4K_2WO_4 + 6Na_2WO_4 + 2Na_2ZrO_3 + 8CO_2 + 20H_2O.$$

At a bright red heat, there is a further loss of carbonic anhydride.

*Ammonium zirconodecatungstate*, $3(NH_4)_2O,ZrO_2,10WO_3 + 13H_2O$, is

obtained in a similar manner to the corresponding potassium compound, substituting ammonium paratungstate for the potassium salt. It forms small, rhombic crystals, which act strongly on polarised light, and lose their water rapidly in the air, and slowly even in the liquid from which they have separated. Sometimes it separates in lenticular crystals either isolated or in tufts. This substance is very soluble in water, the solution having an acid reaction to litmus. The methods adopted by the author for the analysis of these compounds are similar to those employed by Marignac for the analysis of the analogous silicotungstates. The zirconodecatungstates are much more unstable than the silicodecatungstates, hydrochloric, sulphuric, and nitric acids immediately precipitating yellow tungstic acid from their solutions, whilst phosphoric acid slowly forms a gelatinous precipitate of zirconium phosphate. On adding ammonia to a solution of the acid ammonium salt described above, a precipitate of zirconia is formed which does not redissolve on expelling the excess of ammonia by boiling. The normal ammonium salt could not therefore be obtained. In this respect, the zirconodecatungstate behaves very differently from the corresponding silicodecatungstate. The chlorides of barium, calcium, and magnesium, and the nitrates of lead, silver, and mercury, give insoluble precipitates with solutions of the zirconodecatungstates.

Gelatinous zirconia does not dissolve in a solution of sodium paratungstate. A. C. C.

**Thorium Compounds.** By JOSEPH LESINSKY and CHARLES GUNDLICH (*Zeit. anorg. Chem.*, 1897, **15**, 81—83).—Thorium bromide, $ThBr_4 + 8H_2O$, is prepared in a pure state by dissolving pure thorium hydroxide, obtained by precipitating the nitrate with ammonia, in freshly distilled hydrobromic acid and evaporating the solution in the dark in a vacuum over sulphuric acid. The product, washed with light petroleum and chloroform, and recrystallised from alcohol, is obtained in large, white, hexagonal prisms, very easily soluble in alcohol and water. It melts at 100° in its water of crystallisation; a comparatively high temperature, however, is necessary to eliminate all the water.

The authors are engaged in the preparation of thorium iodide, chlorate, bromate, and iodate. E. C. R.

**Potassium Sulphantimonites.** By POUGET (*Compt. rend.*, 1897, **124**, 1445—1447).—The normal potassium sulphantimonite, $K_3SbS_3$, is obtained in small, white, very deliquescent crystals by dissolving antimony sulphide in a concentrated solution of the proper proportion of potassium sulphide, and rapidly concentrating the solution out of contact with air. The crystals are soluble in water, and alter rapidly when exposed to air.

The metasulphantimonite, $KSbS_2$, obtained by Ditte in the dry way, can also be prepared from a solution having the composition $Sb_2S_3 + 2K_2S + Aq$. If evaporated in a vacuum in the cold, this solution yields the compound $K_4Sb_2S_5$, but if heated out of contact with air, red, elongated octahedra of the salt $KSbS_2$ separate, whilst the normal sulphantimonite remains in solution. The red crystals are stable when exposed to air, and are insoluble in cold water, by which

they are only very slightly affected; they are, however, decomposed by boiling water, with separation of antimony sulphide.

C. H. B.

**Preparation of Silver Sulphantimonites and Sulpharsenites by a Dry Method.** By HERMANN SOMMERLAD (*Zeit. anorg. Chem.*, 1897, 15, 173—179).—Artificial pyrargyrite, $Ag_3SbS_3$, is obtained by heating a dry mixture of silver chloride with antimony trisulphide in the proportion $3AgCl : Sb_2S_3$, in a retort from which the air has been driven out by carbonic anhydride. The reaction commences at 140°, and antimony trichloride distils over; the mixture is heated for some time at 360°, and then cautiously melted. The product is of a dark lead-colour with a reddish tinge, and has a radial fracture; it gives a dull-red streak, and a dark, cochineal-red powder. Under the microscope, in transmitted light, thin splinters are dark reddish-brown, whilst in reflected light they have a strong metallic lustre. The sp. gr. = 5·760 (the sp. gr. of natural pyrargyrite = 5·75—5·85). The chemical behaviour of the artificial compound agrees with that of the natural compound. When strongly heated in a glass tube, it yields a small sublimate of $Sb_2O_3$ and $Sb_2S_3$. The red powder is at first turned black by nitric and tartaric acids, and then dissolves with separation of sulphur, whilst with hydrochloric acid it is partially decomposed with evolution of hydrogen sulphide. Hot potassium hydroxide, ammonium sulphide, and potassium sulphide decompose the compound with precipitation of silver sulphide. It is not decomposed by ammonia.

Artificial miargyrite, $AgSbS_2$, is obtained in a similar manner by heating a mixture of silver chloride and antimony trisulphide in the proportion $3AgCl : 2Sb_2S_3$; the reaction commencing at 110°. The product is a lustrous black mass with a conchoidal fracture very similar to melted natural miargyrite. It gives a black streak, and a lustrous black powder. The sp. gr. = 5·200 (the sp. gr. of natural miargyrite = 5·184—5·4). The chemical behaviour of the compound agrees with that of the natural compound.

The author was unable to prepare artificial stephanite and polyargyrite by this method, although they are easily prepared by heating a mixture of their constituents.

Artificial proustite $Ag_3AsS_3$ is obtained by heating a mixture of silver chloride and arsenic sulphide in the proportion $3AgCl : As_2S_3$. The reaction commences at 150°, and the product is a brittle, reddish-black, lustrous mass having a radial fracture. It gives a bright red streak and powder, and under the microscope thin splinters appear bright reddish-brown. The sp. gr. = 5·49 (the sp. gr. of natural proustite = 5·5). The author has also prepared the compounds $AgAsS_2$ and $Ag_4As_2S_5$ by this method.

Artificial zinckenite, $PbSb_2S_4$, is obtained by heating a mixture of lead chloride and antimony sulphide.

E. C. R.

**Silver Sulphantimonites.** By POUGET (*Compt. rend.*, 1897, **124**, 1518—1520).—The products of the action of solutions of silver nitrate on solutions of potassium sulphantimonite (preceding page) vary with the concentration of the solutions, the proportions of the reacting substances, and the temperature. With dilute solutions and

an excess of the sulphantimonite, the product is an amorphous, black precipitate of normal silver sulphantimonite, $Ag_3SbS_3$. If, however, the solution contains not less than 0·29 of a gram-molecule of the sulphantimonite per litre, and only a small proportion of silver nitrate is added, the black precipitate is converted into a yellow, crystalline one of the composition $Ag_2KSbS_3$, and this conversion continues until the proportion of unaltered sulphantimonite left in the solution reaches the limit specified. This double sulphantimonite is at once converted into the normal silver salt by the action of silver nitrate. The double salt is also obtained by the action of excess of potassium sulphantimonite on silver sulphite; it is decomposed by alkali sulphides, with separation of silver sulphide, and when boiled with water, splits up into the normal potassium salt and the normal silver salt, the latter under these conditions being crystalline, lustrous, and reddish in colour.

When an excess of silver nitrate is added to the alkali sulphantimonite, the precipitate is always black, and contains more silver sulphide than corresponds with the formula $Ag_3SbS_3$, the reason being that silver nitrate partially decomposes the sulphantimonite, and the solution always contains some antimony precipitable by hydrogen sulphide. Silver nitrate solution, in fact, decomposes precipitated antimony sulphide, a mixture of silver and antimony sulphides being formed. All the silver is precipitated and antimony passes into solution. C. H. B.

---

## Mineralogical Chemistry.

**Platinum.** By W. J. Martin, Junr. (*16th Ann. Rept. U.S. Geol. Survey*, for 1894–5, Pt. III, 1895, 628—633).—This paper contains the results of the mineralogical examinations of platinum from numerous localities; seventeen analyses are given of crude material, and nine of iridosmine obtained from crude platinum. No relation can be traced between the magnetic properties of the grains and the amount of iron shown in the analyses, some of the samples poorer in iron being more magnetic than those containing more iron. Samples from the same region differ widely in composition; for example, from Colombia, S.A., 38—90; Russia, 49—84 per cent. of platinum; Oregon, 24—94 per cent. of iridosmine. L. J. S.

**Asphaltic Rocks and the Origin of Asphaltum.** By Stanislas Meunier (*Compt. rend.*, 1896, **123**, 1327—1329).—The asphaltum of bituminous rocks is completely dissolved out by digesting the powdered rock with carbon bisulphide; this affords a ready method for determining the amount of asphaltum present. A bituminous rock from Travers in Neuchâtel has been examined in this way. Numerous so-called bituminous rocks from various localities, including oil-shales, coals, &c., in which fossils are often present, were found to contain no asphaltum, there being nothing which could be dissolved out by carbon

bisulphide. Since, in the latter case, the carbonaceous matter is of organic (animal and vegetable) origin, it is concluded that true asphaltum is of deep seated origin, and is the result of purely mineral reactions of the type of the double decomposition of metallic carbides and water.
L. J. S.

**Roumanite [Rumänite].** By Constantin I. Istrati (*Bul. Soc. Sci., Bucarest*, 1897, **6**, 55—59. Compare Abstr., 1894, ii, 457).—The amber-like resin, called roumanite, has been found in a bed of ozocerite, at Mosori, north of Tîrgu-Ocna, in Moldavia. It is of a yellow colour with a tinge of green, and in parts dark; it is hard and not friable, and has a conchoidal fracture; analyses gave the results under I. A black, bituminous variety from Buzĕŭ district, in Moldavia, contained C, 81·17; H, 13·28; sp. gr. = 0·9988, this being lower than that of other varieties (sp. gr. = 1·09—1·119). The other analyses of Moldavian roumanite are quoted from the author's previous papers (*Bul. Soc. Sci. Fizice*, 1895, **4**, 59—77; *Anal. Acad. Române*, 1895, **16**).

| | C. | H. | O [diff.]. | S. | Ash. |
|---|---|---|---|---|---|
| I. Yellow ............ | 83·319 | 10·659 | 3·88 | 1·72 | 0·4185 |
| Blackish-yellow ... | 77·79 | 10·76 | 9·98 | 1·29 | 0·18 |
| Reddish ............ | 79·81 | 10·31 | 8·21 | 1·33 | 0·52 |
| Blackish-yellow ... | 81·28 | 10·48 | 6·13 | 1·47 | 0·64 |
| Yellow ............ | 81·68 | 9·80 | 6·40 | 1·27 | 0·85 |
| Black ............... | 83·29 | 10·77 | 4·45 | 0·93 | 0·56 |
| Black, bituminous | 81·17 | 10·39 | 6·63 | 1·10 | 1·00 |
| Garnet red ......... | 82·07 | 11·11 | 5·20 | 0·93 | 0·69 |

L. J. S.

**Ozocerite from Moldavia.** By Constantin I. Istrati (*Bul. Soc. Sci., Bucarest*, 1897, **6**, 61—93).—An exhaustive account is given of Moldavian ozocerite. It occurs in beds $\frac{1}{4}$—$\frac{1}{2}$ metre thick in Miocene sandstone, and is of wide distribution. When first dug out, it is pale yellow and soft, like wax, but on long exposure to the air it becomes heavier, more compact, and darker in colour, then giving a greenish streak; these changes are due to the loss of volatile hydrocarbons. The original characters are retained in the interior of large specimens. Previous analyses are collected together, and several new ones added. The following varieties are distinguished :—

| | C. | H. | Sp. gr. | Melting point. |
|---|---|---|---|---|
| Ozocerite proper | 84 —86 | 13·5—14·5 | 0·85—0·93 | 61— 65·5° |
| Pietricikite ...... | 84 —85 | 14 —15 | 0·94—0·95 | 82— 90 |
| Moldovite ...... | 84·5—85 | 14 —15 | 0·96—0·97 | 95—100 |

*Moldovite* is a new name for the variety from Mosori, north of Tîrgu-Ocna; it differs in appearance from the other varieties, and has a higher sp. gr. and melting point. *Pietricikite* is the correct spelling of Dana's zietrisikite.
L. J. S.

**Marcasite, &c., Pseudomorphous after Pyrrhotite.** By Alfred Lacroix (*Compt. rend.*, 1897, **125**, 265—267).—The marcasite which occurs on the fibrous blende at Pontpéan mine, near Rennes, Dept. Ille-et-Vilaine, is described, and four types of crystals

distinguished. With it are hexagonal plates, which are pseudomorphs of marcasite, or of marcasite, pyrites, and galena after pyrrhotite. The crystals of these minerals are arranged in certain regular positions with respect to the pyrrhotite forms. L. J. S.

**Bournonite from Isère.** By PIERRE TERMIER (*Bull. Soc. fran. Min.*, 1897, **20**, 101—110).—Bournonite was formerly found with galena in a quartz and dolomite vein in a coal mine at Peychagnard, Isère. Analysis by Pisani of crystallised material gave

| S. | Sb. | Pb. | Cu. | As. | Fe, Ag. | Total. |
|---|---|---|---|---|---|---|
| 20·2 | 24·7 | 40·0 | 13·7 | trace | nil | 98·6 |

Sp. gr. = 5·78. A detailed description is given of two crystals, and six new forms are noted. L. J. S.

**Sylvanite from Kalgoorlie.** By AUGUST FRENZEL (*Tsch. Min. Mitth.*, 1897, **17**, 288—289).—Sylvanite occurs in schistose rocks in more than one mine in the auriferous district about Kalgoorlie, Hannan's district, Western Australia. It is silvery white with metallic lustre, and has a perfect cleavage in one direction. $H = 2\frac{1}{2}$; sp. gr. = 8·14. The analysis agrees with the formula $(Au,Ag)Te_2$.

| Te. | Au. | Ag. | Total. |
|---|---|---|---|
| 58·63 | 36·60 | 3·82 | 99·05 |

An iron-black telluride of gold and silver with conchoidal fracture and no cleavage also occurs here. L. J. S.

**[Scheelite, Tetradymite, Altaite, Stromeyerite, Danaite, &c., from Canada.]** By G. CHRISTIAN HOFFMANN (*Rept. Geol. Survey, Canada*, 1897, **8** (1895), R, 1—59).—*Scheelite.*—Massive scheelite of a light smoke-grey colour occurs with mispickel and pyrites in a quartz vein in the Malaga gold mining district, Queen's Co., Nova Scotia. Analysis gave

| $WO_3$. | CaO. | $CO_2$. | Insol. | Total. | Sp. gr. |
|---|---|---|---|---|---|
| 79·01 | 19·80 | 0·71 | 0·11 | 99·63 | 6·002 |

*Tetradymite.*—This occurs with altaite and hessite near Liddel Creek in the West Kootenay district, British Columbia. It has a foliated structure, the colour being lead-grey to steel-grey. The streak is black. Analysis gave

| Te. | S. | Se. | Bi. | Pb. | Ag. | Tl. | Insol. (quartz). | Total. | Sp. gr. |
|---|---|---|---|---|---|---|---|---|---|
| 36·01 | 4·30 | trace | 51·85 | 3·50 | 0·91 | trace | 3·52 | 100·09 | 7·184 |

Deducting quartz, altaite, and hessite, this gives the formula

$$2Bi_2Te_3,Bi_2S_3.$$

*Altaite.*—Massive altaite occurs with hessite, gold, copper, &c., in a quartz vein at Long Lake, Yale district, British Columbia. It is tin-white, with sometimes a bronze-yellow tarnish. Analysis gave

| Te. | Pb. | Ag. | Fe. | Au (free). | Insol. (quartz). | Total. | Sp. gr. |
|---|---|---|---|---|---|---|---|
| 39·57 | 49·72 | 2·09 | 0·63 | 0·01 | 7·84 | 99·86 | 8·081 |

This corresponds with 87·46 per cent. of altaite, with some hessite, and apparently 8·24 per cent. of native tellurium. Analysis of the

associated hessite gave Te, 37·33; Ag, 60·68; Au, 2·29 = 100·30 per cent. Petzite, also from the Yale district, was found to contain 23·10 and 18·79 per cent. of gold.

*Stromeyerite.*—With bornite, chalcopyrite, galena, argentite, &c., from Toad Mtn., West Kootenay district, B.C. Massive, with subconchoidal fracture. Colour, dark steel-grey. Streak, dark grey and shining. Analysis gave

| S. | Ag. | Cu. | Fe. | Total. | Sp. gr. |
|---|---|---|---|---|---|
| 15·74 | 52·27 | 31·60 | 0·17 | 99·78 | 6·277 |

*Danaite.*—This occurs massive with pyrrhotite, mispickel, and pyrites at Monte Cristo Mtn., West Kootenay district, B.C. The colour is silver-white. Analysis gave

| As. | S. | Fe. | Co. | Insol. (quartz). | Total. | Sp. gr. |
|---|---|---|---|---|---|---|
| 46·41 | 19·21 | 28·91 | 2·97 | 3·86 | 101·36 | 6·166 |

The above analyses, in each case the mean of two, are by R. A. A. Johnston. The specific gravities given have been corrected for contained quartz. The report also includes analyses of limestones, dolomites, coals, iron ores, nickeliferous pyrrhotites, waters, &c., as well as numerous gold and silver assays. L. J. S.

**[Coral Limestones from Florida.]** By EDMUND OTIS HOVEY (*Bull. Mus. Comp. Zool. Harvard Coll.*, 1896, **28**, 63—91).—Several analyses, by G. Steiger, are given of coral limestones from the artesian well borings at Key West, Florida. The limestones have an oolitic structure, and contain particles of quartz sand.

L. J. S.

**[Origin of Iron Ores.]** By L. DE LAUNAY (*Compt. rend.*, 1897, **124**, 689—692; and *Ann. des Mines*, 1897, **12**, 178—185).—Large masses of iron carbonate have been supposed to have been deposited as such from water; the author, however, considers them to have been formed by the action of limestones on iron salts derived from iron sulphide. In support of this view, it is pointed out that, whilst deposits of iron sulphide always occur in schists, those of iron carbonate always occur in limestones. By the surface oxidation of the carbonate, deposits of oxides are formed. L. J. S.

**A Mineral allied to Pinakiolite from Långban.** By HELGE BÄCKSTRÖM (*Jahrb. f. Min.*, 1897, i, 243, Ref.; from *Geol. Fören. i Stockholm Förh.*, 1895, **17**, 257).—The mineral is found with hausmannite, a brownish arsenate, and sometimes pinakiolite, in the granular dolomite of Långban, Sweden; it is iron black with metallic lustre, and occurs in broken, striated prisms of rhombic outline with an angle of 68° 36½′; the forms {120} and {210} are also present. There is no cleavage; sp. gr. = 3·935; H = 6. Very thin sections are transparent, and of a dark reddish-brown colour; the extinction is straight, and the *c* axis is the direction of greatest absorption. It is soluble in hydrochloric acid with evolution of chlorine. Analysis gave:

| $B_2O_3$. | $Fe_2O_3$. | MnO. | O. | CaO. | PbO. | MgO. | $SiO_2$ | Total. |
|---|---|---|---|---|---|---|---|---|
| 13·92 | 10·52 | 46·95 | 3·45 | 1·35 | 1·22 | 22·36 | 0·78 | 100·55 |

This composition is like that of pinakiolite, but, although the mineral is orthorhombic, the crystallographic characters are different. More material is to be examined before a new name is given.

L. J. S.

**Crystallised Mineral formed in Leaden Coffins.** By ALFRED LACROIX (*Compt. rend.*, 1897, **124**, 419—422; and *Bull. Soc. fran. Min.*, 1897, **20**, 112—118).—Two leaden coffins, dated 1630, have recently been dug up in Paris; the contained skeletons are in part thinly incrusted with needles and plates of a substance which is referred to metabrushite ($H_2Ca_2P_2O_8 + 3\frac{1}{2}H_2O$). The white, acicular crystals are best developed in the interior of the skull, where they attain a length of 8 mm. Material, which, however, could not be completely separated from organic matter, lost 25·50 per cent. on ignition. The sp. gr. of the pure crystals is 2·31. The crystals are monosymmetric, and are flattened, and have a perfect cleavage, parallel to the plane of symmetry; the optic axial plane and obtuse bisectrix are perpendicular to the plane of symmetry; $2V_a = 81°$; optically negative. Some of these characters are in agreement with brushite ($H_2Ca_2P_2O_8 + 4H_2O$), so that the reference to metabrushite is not beyond doubt.

The mode of formation of this substance must have been the same as that described by Gautier (Abstr., 1893, ii, 536; 1896, ii, 185). Ammonium phosphate, produced by the decomposition of organic matter, especially the brain, acting on the calcium carbonate of the bones, would give rise to calcium phosphate. These reactions, taking place within the body itself, furnish a case of "automineralisation."

L. J. S.

**Synthesis of Hanksite.** By AUGUST BENJAMIN DE SCHULTEN (*Compt. rend.*, 1896, **123**, 1325—1327).—When a hot solution of caustic soda (50 grams in 90 c.c. water) is poured into a hot solution of sodium sulphate and carbonate (20 grams $Na_2SO_4,10Aq$ and 0·8 gram $Na_2CO_3$ in 30 c.c. water), a crystalline precipitate, having the properties of natural hanksite, is formed; the crystals are freed from caustic soda by washing with alcohol. Unless these details are followed, thenardite is also formed. The analyses of the crystals, which are of sp. gr. 2·613, agree closely with the formula originally given for the natural mineral, namely, $4Na_2SO_4,Na_2CO_3$, and not with that recently proposed by Pratt (this vol., ii, 49). The crystals are hexagonal prisms measuring 0·05 × 0·03 mm., with the forms $c\{111\}$, $m\{2\bar{1}\bar{1}\}$, and sometimes $r\{100\}$ and $p\{13.1.1\}$. They are optically negative, and show optical anomalies; viewed in parallel polarised light through the basal plane, 6 or 12 sectors are seen, and through the prism planes 4 sectors. When crystals are slowly grown from a cold solution, no optical anomalies make their appearance; such crystals may be easily formed by allowing a concentrated solution of sodium sulphate and carbonate, with less caustic soda than in the previous case, to evaporate on a microscope slide.

L. J. S.

**Isometric Crystals of Silica.** By KONSTANTIN VON CHRUSTSCHOFF (*Jahrb. f. Min.*, 1897, i, 240 Ref.; from *Bull. Acad. Sci. St. Pétersbourg*, 1895, [v], **2**, 27—33).—An aqueous solution of silica, with a little

hydrogen borofluoride to act as a mineraliser, was heated for 5 hours in a sealed platinum vessel with the following results.

| | | | |
|---|---|---|---|
| 1. At 180° | (=10 atmos.). | No change. |
| 2. „ 180—228° | (=26 atmos.). | Isometric crystals. |
| 3. „ 228—235° | (=30 „ ). | No quartz. |
| 4. „ 240—300° | (=86 „ ). | Quartz. |
| 5. „ 310—360° | (=189 „ ). | Tridymite and some quartz. |

The colourless transparent, isometric crystals show the forms $o\{111\}$, $a\{100\}$, and $d\{110\}$ in various combinations, and are twinned on the spinel law. They are perfectly isotropic, and have an index of refraction of about 1·58. Sp. gr. = 2·412. They are soluble in hydrofluoric acid; analysis gave 99·78 per cent. $SiO_2$. The crystals most resemble cristobalite, which is isotropic at 170°. L. J. S.

**Formation of Zeolites.** By Alfred Lacroix (*Compt. rend.*, 1896, 123, 761—764).—Owing to the frequent occurrence of zeolites in volcanic rocks, it was formerly supposed that an elevated temperature was necessary for their production. But Daubrée and Bouis have described the formation of numerous zeolites by the action of hot springs having a temperature considerably below 100°; and phillipsite has been found in the deep-sea dredgings of the *Challenger*. Further, in the Pyrénées, zeolites are found in mineral veins, and in plutonic and sedimentary rocks. The present paper describes the formation of zeolites by the action of almost pure water, at the temperature of melting snow, on basic felspathic rocks.

In several elevated districts in the Pyrénées, in the beds of streams, or where the shattered and decomposed rocks are exposed to the action of running water derived from the melting of the snow, zeolites (chabazite, stilbite, and laumontite) are abundant, impregnating the rocks, or coating surfaces and cementing together fragments. These alterations take place in rocks, both plutonic and metamorphic, which contain basic plagioclases and dipyre, these minerals affording the necessary material for the formation of lime and soda-lime zeolites.

L. J. S.

**Beryl in a Pseudomorph after Beryl.** By Arvid G. Högbom (*Jahrb. f. Min.*, 1897, i, 431, Ref.; from *Geol. Fören. i Stockholm Förh.*, 1895, 17, 412—414).—A large hexagonal prism, which was probably originally a crystal of beryl, consists of an irregular aggregate of beryl crystals with some chlorite, kaolin, and perhaps muscovite; in cavities, there are well developed crystals of beryl, the larger of a straw-yellow colour and the smaller water-clear. In these crystals, there are elongated cavities containing two liquids (one of which is probably carbonic anhydride), and bubbles of gas. Analysis of the beryl by G. Lundell gave

| $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | BeO. | CaO. | MgO. | Alkalis. | Loss on ignition. | Total. |
|---|---|---|---|---|---|---|---|---|
| 65·14 | 21·72 | trace | 11·55 | 0·32 | 0·30 | trace | 1·64 | 100·67 |

Sp. gr. = 2·6. The loss on ignition is mostly due to the fluid enclosures. It seems that here the original beryl material has been altered and beryl again formed. L. J. S.

**Edingtonite from Böhlet, Sweden.** By GUSTAF LINDSTRÖM (*Öfvers. k. Vetensk.-Akad. Förh. Stockholm*, 1896, **53**, 469—472. Compare this vol., ii, 328).—The following analysis (I) is given of the edingtonite crystals recently found at the manganese mines of Böhlet, Vestergöthland; sp. gr. 2·782. Under II, is the analysis published by Heddle in 1855 of the Scotch mineral.

| | $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | BaO. | CaO. | MnO,MgO. | $Na_2O$. | $K_2O$. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|
| I. | 36·37 | 20·06 | 0·04 | 29·99 | 0·16 | 0·06 | 0·20 | 0·21 | 13·12 | 100·21 |
| II. | 36·98 | 22·63 | — | 26·84 | trace | — | trace | — | 12·46 | 98·91 |

Anal. I gives the ratios, $Al_2O_3$ : BaO(CaO and alkalis) : $SiO_2$ : $H_2O$ = 1 : 1·04 : 3·06 : 3·70. A trace of chlorine is present, but no fluorine, strontium, or lithium. Most of the 0·06 per cent. of MnO,MgO is due to enclosed manganese ore; the pure mineral contains only a trace of magnesium, and neither iron nor manganese. At 100°, there is a loss of 3·82; at 155°, of 5·90, and at 230°, of 7·90 per cent.; if the mineral has not been too strongly heated, this water is reabsorbed with decrepitation, the material being transformed into a woolly mass consisting of fine needles. A second determination of the total water gave 13·08 per cent. L. J. S.

**Constitution of Analcite.** By CHARLES LEPIERRE (*Bull. Soc. Chim.*, 1896, [iii], **15**, 561—565).—Analcite, differing from the ordinary mineral in optical properties and crystalline form (as determined by Bensaude), gave the following results on analysis.

| $SiO_2$. | $Al_2O_3$. | CaO. | $Na_2O$. | $H_2O$. | Total. |
|---|---|---|---|---|---|
| 54·29 | 23·30 | 0·31 | 13·84 | 8·36 | 100·10 |

This agrees closely with the usual formula, $Na_2O,Al_2O_3,4SiO_2 + 2H_2O$. The mineral was free from calcite, and titanium and potassium were absent. About half (3·90 per cent.) of the water is lost at 200°, the remainder being expelled at 440°; over sulphuric acid, or at 100°, there is no loss. To express the difference in the behaviour of the two molecules of water, a structural formula is given, the mineral being considered as a salt of diorthosilicic acid, $H_6Si_2O_7$. This formula is simpler than that recently proposed by Clarke (Abstr., 1894, ii, 459). L. J. S.

**[Analysis of Ilvaite.]** By K. H. SCHNERR (*Jahrb. f. Min.*, 1897, i, 432 Ref.; from *Inaug.-Diss. München*, 1894. Compare this vol., ii, 106, 147).—The methods employed in the analysis of several garnets are described in detail in the dissertation (but not in the abstract quoted), especially the estimation of ferrous and ferric iron by decomposing the mineral with potassium iodide and sulphuric acid, and then volumetrically determining the separated iodine. This method was tested on ilvaite (of which the complete analysis is given below) and magnetite.

| $SiO_2$. | FeO. | $Fe_2O_3$. | MnO. | CaO. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|
| 29·42 | 34·13 | 21·29 | 0·30 | 13·41 | 1·71 | 100·19. |

L. J. S.

**Fayalite.** By GEORGE OTIS SMITH (*Johns Hopkins Univ. Circulars*, 1894, **13**, 82).—Fayalite, in perfect skeleton crystals of tabular habit, from the surface of a crystallised iron slag, gave $a : b : c$ =

0·4632 : 1 : 0·5835. An analysis of the crystals, by T. L. Blalock, agrees with the formula $Fe_2SiO_4$.

| $SiO_2$. | FeO | CaO. | MgO. | Total. |
|---|---|---|---|---|
| 30·10 | 68·43 | 0·57 | 0·13 | 99·23 |

L. J. S.

**Action of Volcanic Fumaroles on Serpentine.** By ALFRED LACROIX (*Compt. rend.*, 1897, **124**, 513—516).—In the ravine of Sasaki, near Kalamaki in the Gulf of Corinth, serpentine is overlain by Pliocene limestones; and at the contact between these are volcanic fumaroles which give off water vapour charged with hydrogen sulphide and carbonic anhydride. The limestone is converted into gypsum; and the serpentine, by the elimination of magnesium and iron in the form of epsomite and melanterite, is finally converted into opal or quartz and chalcedony. This opal preserves the original minute structure of the rock, and in it the original grains of picotite are sometimes embedded. The less completely altered rock contains epsomite, melanterite, marcasite and native sulphur, and, as secondary products derived from the marcasite, various basic ferric sulphates. The acid rocks (rhyolites, &c.) of the same district are reduced by solfataric action to the same end-product, here, however, with the production of various aluminium and alkali sulphates. L. J. S.

**[Chrome-diopside, Hornblende and Pleonaste from Montana.]** By GEORGE P. MERRILL (*Proc. U.S. National Museum,* 1895, **17**, (1894), 637—673).—In a paper describing a collection of eruptive rocks from Gallatin, Jefferson, and Madison Counties, Montana, the following mineral analyses are given.

Augite, in small green crystals from a rock related to olivine-basalt near Bozeman, gave analysis I (by L. G. Eakins) showing it to be a chrome-diopside. Dark green hornblende, which, with hypersthene, forms pyroxenite between Meadow and Granite Creeks, gave II. Dark green pleonaste, occurring abundantly in a similar pyroxenite, gave III (Eakins); sp. gr. 3·89.

| | $SiO_2$. | $Cr_2O_3$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MnO. | CaO. | MgO. | $K_2O$. | $Na_2O$. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I. | 52·50 | 1·07 | 2·26 | 2·05 | 2·47 | trace | 21·70 | 17·11 | 0·07 | 0·35 | 0·64 | 100·22 |
| II. | 46·14 | — | 17·07 | 8·45 | not det. | — | 11·70 | 15·01 | 0·10 | 1·11 | — | 99·58 |
| III. | 0·55 | 2·62 | 62·09 | 2·10 | 17·56 | trace | 0·16 | 15·61 | — | — | — | 100·69 |

L. J. S.

**Jadeite from "Tibet."** By MAX BAUER (*Jahrb. f. Min.*, 1897, i, 258—259. Compare Abstr., 1896, ii, 310).—The presence of nephelite in the jadeite from "Tibet," described in the previous paper (*loc. cit.*), suggested that nephelite might be a constituent of crystalline schists as well as of igneous rocks: this is now confirmed by the presence of some chlorite-schist on one of the new specimens examined by the author. Chemical and optical tests of this chlorite were made. L. J. S.

**[Augite from Madras.]** By THOMAS H. HOLLAND (*Quart. Journ. Geol. Soc.*, 1897, **53**, 405—419).—In a petrological paper, the following analysis (I) is given of pale brown augite, which, with a plagioclase near labradorite, and a ground-mass of micropegmatite, forms an augite-diorite dyke at the Seven Pagodas, Chingelput district, Madras Presidency. The bulk analysis of the rock is given under II.

| | $SiO_2$. | $TiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MnO. | CaO. | MgO. | $Na_2O$. | $K_2O$. | $H_2O$. | $P_2O_5$. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I. | 50·02 | — | 5·61 | 15·61 | — | trace | 14·84 | 12·01 | 0·96 | | 0·76 | — | 99·81 |
| II. | 51·15 | 0·44 | 15·92 | 9·34 | 2·87 | 0·09 | 10·40 | 6·48 | 1·19 | 1·61 | 0·11 | 0·06 | 99·66 |

L. J. S.

**American Kaolins.** By Charles Frederic Mabery and Otis T. Klooz (*Journ. Amer. Chem. Soc.*, 1896, **18**, 909—915).—Eleven analyses are given of American pottery clays; these are compared with the best German and English china clays. They all contain free silica, 1·33—80·30 per cent. The purest kaolin, from Woodbridge, Middlesex Co., N.J., gave

| $SiO_2$. | $Al_2O_3$. | Iron. | CaO. | MgO. | $K_2O$. | $Na_2O$. | Combined $H_2O$. |
|---|---|---|---|---|---|---|---|
| 44·34 | 38·09 | 0·15 | 0·96 | 0·10 | 1·00 | 0·79 | 14·34 |

L. J. S.

**Meteoric Iron.** By Emil W. Cohen (*Jahrb. f. Min.*, 1897, i, 254—255 Ref.; from *Ann. k.k. naturhist. Hofmuseums*, 1895, **10**, 81—93).—In No. IV. of his "Meteoric Iron Studies," the author gives the results of the examination of the magnetic characters and specific gravity of numerous irons.

Most irons may easily be strongly permanently magnetised; when this is not the case, the iron has been heated and slowly cooled. All irons, when strongly heated and quickly cooled, become magnetic, and this magnetism is retained for some time. Tænite behaves as meteoric iron, but cohenite and schreibersite are rather less easily magnetised.

In general, irons having the same chemical composition have much the same specific gravity; and the specific gravities calculated from the composition do not vary much from the observed values. Hexahedral iron has an average sp. gr. of 7·80—7·88, and in octahedral iron the sp. gr. varies from 7·78 to 7·86, being greater when the lamellæ are finer, and when more nickel is present. L. J. S.

**River Waters of Bohemia.** By Joseph Hanamann (*Jahrb. f. Min.*, 1897, i, 289—291 Ref.; from *Archiv naturw. Landes. Böhmen*, 1894, **9**, No. 4, 102 pp.).—Numerous analyses are given of the waters of the River Eger and its tributaries. These show the variation in the mineral constituents of waters collected from different geological formations, for example, from phyllites, granites, basalts, &c. Analyses of water, taken from several points between the source and the mouth of the river, show that almost all the bases and acids, with the exception of silica, increase in amount towards the mouth. The total solids vary at different seasons of the year. The composition of the water of the Eger is compared with that of other rivers. L. J. S.

**Water from Wells in the Nubian Desert.** By Emily A. Aston (*Quart. Journ. Geol. Soc.*, 1897, **53**, 374—375).—As an appendix to a paper by H. G. Lyons on the geology of a portion of the Nubian Desert, the following analyses are given of water from the wells sunk in the sand-and-gravel detritus of the Desert. I, Murrat Wells. II, Bir Tilat Abda, called by the Arabs a 'bitter' well. III, Bir Ab Araga.

| | $SiO_2$. | $Fe_2O_3+Al_2O_3$. | Ca. | Mg. | Na. | K. | $SO_4$. | Cl. | $NO_3$. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|
| I. | 1·28 | 0·26 | 37·76 | 5·81 | 61·38 | 32·08 | 175·23 | 61·79 | 1·86 | 377·45 |
| II. | 3·36 | 4·36 | 31·19 | 6·74 | 63·88 | 30·41 | 182·52 | 21·42 | 1·88 | 345·76 |
| III. | 2·48 | 0·96 | 37·95 | 6·89 | 21·91 | 11·18 | 142·47 | 28·05 | trace | 251·89 |

'Total solid matter' found by direct evaporation, 410·5, 359·5, 253·5; $CaCO_3,H_2CO_3$, 82·04, 28·79, 10·56 respectively. The above results are in grains per gallon. Free ammonia, 0·378, 0·105, 0·199; albuminoid ammonia, 0·185, 0·173, 0·260, respectively, in parts per million. L. J. S.

**Mineral Water from Pennsylvania.** By A. E. Robinson and Charles Frederic Mabery (*Journ. Amer. Chem. Soc.*, 1896, 18, 915—918).—Mineral springs having therapeutic qualities occur in the north-western portion of Pennsylvania; the following analyses are of waters from Conneautville, in Crawford Co. Water from surface springs at this place, which are representative of the springs of the region, gave, in grains per gallon; $K_2CO_3$, 0·985; $Li_2CO_3$, 0·002; NaCl, 0·925; $CaH_2(CO_3)_2$, 2·879; $CaSO_4$, 1·291; $MgCl_2$, 0·204; $FeCO_3$, 0·743; $SiO_2$, 0·233; $H_2S$, trace; total solids, 6·586. Sp. gr., 1·0002 at 20°.

Bittern water from a boring 2,667 feet in depth gave, in parts per 100,000: KCl, 755·6; LiCl, 80·3; AmCl, 216·6; NaCl, 14,430·0; KBr, 245·7; KI, 2·96; $MgCl_2$, 3096·0; $CaCl_2$, 11,880·0; $CaSO_4$, 11·1; $FeCO_3$, 163·5; $AlCl_3$, 31·1; $SiO_2$, 4·6; $H_2S$, 0·05; total solids, 30,536. Sp. gr., 1·205 at 15°. This water is remarkable on account of the presence of large amounts of ammonium chloride, potassium iodide, and lithium. Cæsium and rubidium are absent. L. J. S.

## Physiological Chemistry.

**Action of Albumoses and Peptones in Intravascular Injections.** By Edmond Fiquet (*Compt. rend.*, 1897, 124, 1371—1374).—Peptones prepared in the usual way were dissolved in a small quantity of water, the albumins, albumoses, and albumotoxins precipitated by ammonium sulphate, and alcohol added until the alcoholic strength of the liquid was 68—70°. The filtrate was then concentrated, dialysed, and the peptones precipitated by strong alcohol.

Albumoses, prepared by the action of pancreatic juice on beef, were purified by first adding to their concentrated solution sufficient alcohol to bring its strength up to 50°, and then mixing the filtrate with a further quantity of alcohol to bring its strength up to 66—88°, when the albumoses were precipitated.

The albumoses and peptones thus purified were injected into dogs and rabbits in quantities amounting in some cases to as much as 7·7 grams per kilogram of body weight at one injection, whilst in others the injections were repeated on several successive days. No injurious effects were observed; the coagulation of the blood was not prevented and there was neither narcosis nor tremors. The author

concludes that the poisonous effects generally attributed to albumoses and peptones are really due to albumotoxins, ptomaines, &c., which have not been completely removed in the process of purification.

C. H. B.

**Behaviour of some Varieties of Sugar in the Animal Organism.** By Fritz Voit (*Bied. Centr.*, 1897, **26**, 384—385; from *Neue Zeits. Zuckerind.*, 1896, 309).—Dextrose and levulose are both sugars which produce glycogen; whether galactose belongs to the group is doubtful, but, in any case, it is much less favourable to the production of glycogen than are dextrose and levulose. Formation of glycogen from di- and poly-saccharides depends on their behaviour in the intestinal canal, where they are decomposed into simple sugars which may, or may not, belong to the class which yields glycogen.

Cane-sugar is inverted, in the intestinal canal, into dextrose and levulose from which glycogen is produced. Maltose behaves similarly, whilst the behaviour of lactose is not yet established.

The migration of the various sugars to the urine also depends on the fermentability and production of glycogens. Whilst grape-sugar, which ferments readily, must be consumed in large quantity to show sugar in the urine, a separation of sugar takes place after very small doses of sorbose, which does not ferment.

Experiments with animals, in which sugars were injected subcutaneously, showed that dextrose and levulose produced glycogen, whilst with cane-sugar and lactose there was only a slight formation of glycogen. Further experiments showed that dextrose, levulose, and galactose did not appear in human urine, being rapidly decomposed in the organism. When the disaccharides, saccharose, and lactose were injected, the whole amount was recovered in the urine, whilst maltose disappeared. It is supposed that maltose is either attacked by the cells, or else that it is converted, in the liver, into glycogen either directly or indirectly.

N. H. J. M.

**Composition of Milk and Milk Products.** By Henry Droop Richmond (*Analyst*, **22**, 1897, 93—95).—The author gives the average composition of 11,633 samples of milk taken from railway churns on arrival at the depôts of the Aylesbury Dairy Co. during 1896.

The results again show that the non-fatty solids are fairly constant, varying from 8·7 to 9·1 per cent. In a few instances, they were as low as 7·5 to 8·4 per cent., but in such abnormal milks, which are rarely met with, the ash is much higher than would have been the case if the deficiency in non-fatty solids had been caused by watering. The lowest fat recorded is 3·40 per cent.

Analyses of cream and butter are also given. L. de K.

**Colostrum Fat.** By Robert Eichloff (*Bied. Centr.*, 1897, **26**, 385—386; from *Milchztg.*, 1897, No. 5, 67).—The fat was separated in the following manner:—The colostrum was well mixed with water (3 parts), left for eighteen hours, and the creamy layer removed. This was kept at 4°, for 8 hours, and churned for 35 minutes, after which the butter was washed as usual. The butter was of a deep golden colour, of almost waxy consistency, had an unpleasant odour and taste,

and melted at 35°. In composition, it resembled ordinary butter except that the percentage of proteids (1·71) was higher, and the percentage of ash (0·05) lower. By fractional separation with ether, the fat was separated into a white, crystalline mass, comparatively sparingly soluble in ether, and a readily soluble, dark yellow oil, the colouring matter of which the author supposes to be identical with that of urine.

The yield of fat was 70 per cent. of the colostrum. Sp. gr. = 0·8648—0·8665; melting point = 37·6. N. H. J. M.

**Analysis of Urine: Thermo-optically Positive and Negative Diabetic Sugar.** By FRÉDÉRIC LANDOLPH (*Compt. rend.*, 1897, **125**, 118—119).—Diabetic urine ferments with great rapidity even at the ordinary, or lower, temperatures, and this is characteristic of the true diabetic sugar, the reducing power of which is double that of glucose. This sugar is thermo-optically positive, and when its solution is boiled, the rotatory power is increased, often by several degrees. The quantity of sugar corresponding with the result obtained by fermentation is generally in agreement with that indicated by the polaristrobometer, but the results with Fehling's solution are too high, and are variable and misleading. The cuprous oxide reduced by diabetic sugar differs both in colour and physical condition from that reduced by ordinary glucose.

Diabetic sugar is always accompanied by a certain quantity of a thermo-optically negative sugar, which, like glucose, partially or completely loses its positive rotatory power when its solution is boiled. It ferments much more slowly than the diabetic sugar, but is not identical with glucose; it generally precedes diabetes. C. H. B.

**Formation of Hippuric Acid in the Animal Organism.** By F. W THEODOR C. PFEIFFER and WILHELM EBER (*Landw. Versuchs-Stat.*, 1897, **49**, 97—144).—The results of previous experiments indicated the probable relation between pentoses consumed in food and the formation of hippuric acid (Abstr., 1896, ii, 443).

In the experiments now described, a horse was fed with ordinary food (clover and meadow hay, oats and salt), both alone, and in conjunction with quinine hydrochloride (10 and 20 grams), calomel (3 and 5 grams), and pentoses (500 grams of cherry gum) respectively; during one period the horse was rubbed with mustard spirit (5 per cent., 100 grams per day). During the experiment, which lasted about three and a half months, the amount of water consumed was recorded, and the amount of urine, its sp. gr., the amounts of nitrogen, hippuric acid, sulphuric acid, ethylsulphuric acid, and phosphoric acid were determined each day.

The results of the experiments point to the following conclusions. The decomposition of proteids cannot be the only source of the non-nitrogenous constituents of hippuric acid, whilst the resorbed pentoses have considerable effect in the production of hippuric acid. Interrupted formation of hippuric acid must be attributed either to a reduction of certain hitherto unknown processes of decomposition in the intestines (connected, possibly, with the digestion of cellulose), or else to metabolic processes subsequent to resorption in the intestines.

The pentoses of cherry gum were almost completely digested; this

agrees with the observations of Götze and Pfeiffer (*loc. cit.*) in experiments with sheep. N. H. J. M.

## Chemistry of Vegetable Physiology and Agriculture.

**Fermentation in Solid Materials.** By TH. SCHLOESING, Junr. (*Compt. rend.*, 1897, **125**, 40—43).—In the case of fermentations in solid materials such as soil, farmyard manure, tobacco, and the like, it is commonly observed that the rate of fermentation first increases, then diminishes, and finally the change almost ceases, although the fermentable material is by no means exhausted. If, however, the material is well agitated and broken up, fermentation begins again and the same series of phenomena is observed, and this may be repeated several times.

Examination of the air in contact with the material shows that the cessation of activity is not due to absence of oxygen. Further, if all the gas is pumped out of the material and its pores, and fresh air is admitted, the effect, without agitation and breaking up, is almost *nil*, whilst, on the other hand, agitation has a marked effect on the activity of some anærobic fermentations. It would seem, therefore, that the renewed activity of the ferment is due to the mechanical disturbance and not to aëration, but exactly how the disturbance acts has yet to be ascertained. C. H. B.

**Formation of Diastase.** By WILHELM PFEFFER (*Bied. Centr.*, 1897, **26**, 400—401; from *Ber. Mathem.-phys. Klasse kgl. Sächs. Gesel. Wissens. Leipzig*).—*Penicillium glaucum*, *Aspergillus niger*, and *Bacterium megatherium* were cultivated in liquid media containing the necessary mineral matter, ammonium nitrate, and more or less sugar or other carbon compounds; starch was employed to detect diastase. It was found that the production of diastase diminished with increased amounts of sugar; in the case of *Penicillium glaucum*, diastase ceased to be formed in presence of 15 or 10 per cent. of cane-sugar, and even with 1·5 per cent. the starch was only slightly attacked. Similar results were obtained with *Bacterium megatherium*, whilst *Aspergillus niger* produced diastase even in presence of 30 per cent. of cane-sugar, although in diminished quantity.

With regard to the effect of different sugars in checking the formation of diastase, cane-sugar and dextrose were the most active, maltose less active.

Quinic acid (3—10 per cent.), glycerol, and tartaric acid were without any conspicuous effect on cultivations of *Penicillium glaucum*, and *Aspergillus niger*.

In cultivations containing peptone, instead of ammonium nitrate, greater amounts of sugar are required to check the production of diastase. N. H. J. M.

**Oxidising Action of Manganese Salts: Constitution of Oxydases.** By GABRIEL BERTRAND (*Compt. rend.*, 1897, 1355—1358).—See this vol., ii, 493.

**Action of Guaiacol on the Germination of Spores of Aspergillus fumigatus.** By EM. BOULANGER-DAUSSE (*J. Pharm.*, 1897, [vi], 5, 332—335 and 386—388).—The spores were sown on a sterilised slice of carrot covered with water, or in Raulin's liquid; in the former case, when 7 c.c. of distilled water was present, an addition of 4—5 drops of a 5 per cent. solution of guaiacol in glycerol was capable of preventing all traces of development. In the second series of experiments, when 7 c.c. of Raulin's liquid was used, the addition of 3—4 drops of the same antiseptic solution prevented germination.

J. J. S.

**Composition of Haricots, Lentils, and Peas.** By BALLAND (*Compt. rend.*, 1897, 125, 119—121).—The following results were obtained :—

| | Haricots. | | Lentils. | | Peas. | |
|---|---|---|---|---|---|---|
| | Minimum. | Maximum. | Minimum. | Maximum. | Minimum. | Maximum. |
| Water | 10·00 | 20·40 | 11·70 | 13·50 | 10·60 | 14·20 |
| Nitrogen compounds | 13·81 | 25·16 | 20·32 | 24·24 | 18·88 | 23·48 |
| Fats | 0·98 | 2·46 | 0·58 | 1·45 | 1·22 | 1·40 |
| Sugars and starches | 52·91 | 60·98 | 56·07 | 62·45 | 56·21 | 61·10 |
| Cellulose | 2·46 | 4·62 | 2·96 | 3·56 | 2·90 | 5·52 |
| Ash | 2·38 | 4·20 | 1·99 | 2·66 | 2·26 | 3·50 |

The minimum of nitrogen compounds and maximum of fats in the case of haricots are found only in very large Spanish haricots; with all other varieties, the variations are smaller and are similar to those obtained with peas and lentils. The germs, as in the case of beans, contain a high proportion of nitrogen compounds and very little fat. Egyptian lentils are the richest in nitrogen, and, as a rule, the small varieties of lentils are richer in nitrogen than the large ones. Peas, as Poggiale pointed out, contain the highest proportion of nitrogen before they have reached maturity. Haricots, lentils, and peas have the same acidity as beans; they lose only from 7 to 9 per cent. by decortication; and they undergo no change in chemical composition, even when kept for a long time, although the proportion of water that they will absorb, which at first is about 100 per cent. of their weight, diminishes with their age. C. H. B.

**Composition of Potatoes.** By H. COUDON and L. BUSSARD (*Compt. rend.*, 1897, 125, 43—46).—The potato, after the skin has been removed, consists of three distinct layers, which differ in composition, namely, the cortical layer, the external medullary layer, and the internal medullary layer. The first contains the highest proportion of starch and the lowest proportion of water and nitrogenous matter, the last contains the highest proportion of nitrogenous matter and water and the lowest proportion of starch, whilst the middle layer is intermediate in composition. The proportion of starch in the cortical layer may be twice as great as in the innermost layer, whilst the quantity of nitrogenous matter in the innermost layer may be 28 per cent. more than in the cortical layer, the exact differences varying with the variety of potato.

The culinary value of potatoes is directly proportional to the quantity of nitrogenous compounds and inversely proportional to the quantity of starch that they contain, and may be measured by the ratio between these quantities, the ratio being from 17 to 25 for the best tubers in 1895 and below 8 for the worst. The tendency of the tubers to retain their shape and size when boiled in water, instead of swelling up and becoming floury, is not dependent on the proportion of starch or the size of the starch grains, or on the presence of pectic substances, but is determined by the proteids present. The resistance is greater the higher the proportion of proteids, and is measured by the ratio proteids/starch, the value of this ratio being 14·0 to 8·6 in the most resistant varieties, and from 8·0 to 6·6, or even as low as 4·3, in the varieties that disintegrate most readily.

It follows that, for table purposes, the aim should be to cultivate varieties low in starch and with a thin cortical layer, whilst for industrial purposes, a thick cortical layer and a high percentage of starch are desirable. C. H. B.

**Effect of Manuring Peaty Meadows on the Amount of Water, Potash, and Phosphoric Acid in the Crops.** By H. A. Moritz Fleischer (*Bied. Centr.*, 1897, **26**, 443—447; from *Mitteil. Ver. Förd. Moorkultur.*, 1896, No. 24, 453—462; 1897, No. 7, 129—139).—Application of kainite and phosphates to peaty soil raised the amount of water in the crop by 6 per cent. (average of 4 years). When potash alone was applied, the amount of water in the crop was scarcely changed, and similar results were obtained by the exclusive application of phosphates. The increase in the amount of water is ascribed to increased growth of leguminous herbage, and of varieties of grasses containing more water, in the place of drier grasses, and also to increase in the size of leaves, by which evaporation, and the taking up of water, would be increased. As regards the effect of potash and phosphate manuring on the amounts of these constituents in hay, as compared with the amounts in unmanured hay, the results varied according to the soil. On heavy soil, the percentages were raised as follows:—$K_2O$, 0·32; $P_2O_5$, 0·35 per cent.; on medium soil, the rise was $K_2O = 0·53$, $P_2O_5 = 0·30$ per cent.; on light soil, $K_2O = 0·89$, $P_2O_5 = 0·23$ per cent. In the Rothamsted grass experiments (*Jour. Roy. Agr. Soc. Eng.*, 1858, **19**, 552; 1859, **20**, 228 and 398), the percentage of potash in hay was raised from 1·20 to 1·94 per cent., the percentage of phosphoric acid from 0·29 to 0·44, under the influence of mineral manure including potash and phosphates.

Exclusive application of potash manure increased the percentage of potash in hay from 1·15 to 2·22 per cent., whilst the exclusive application of phosphates lowered the percentage of potash to 1·08. With both manures together, the percentage of potash in the hay did not rise above 1·71.

Phosphatic manure alone increased the percentage of phosphoric acid in the hay from 0·48 to 0·84 per cent.; potash manure alone lowered the percentage to 0·40. With potash and phosphates together, the highest percentage of phosphoric acid in the hay was 0·81.

N. H. J. M.

# Analytical Chemistry.

**Estimation of Carbonic Anhydride in Atmospheric Air, and the Dissociation of Sodium Hydrogen Carbonate.** By ISIDOR ROSENTHAL (*Chem. Centr.*, 1896, i, 1142—1143; from *Sitz.-Ber. Phys. Med. Soc. Erlangen*, **27**, 74—84).—The principle of the method is the measurement of the volume of air required to remove the colour of 20 c.c. of N/1000 soda solution mixed with phenolphthalein. The apparatus is not fully described, but seems to resemble that of Schulz (Abstr., 1892, 533), with the addition of an inclined mirror and the exclusion of side light, by which means the moment of decolorisation is more exactly observed. When the proportion of carbonic anhydride is somewhat above the normal, the decolorisation is sharp, but with 0·04 per cent., the tension of dissociation of the sodium hydrogen carbonate exceeds the partial pressure of the carbonic anhydride in the air, so that complete decolorisation does not occur, and a tint remains which can be imitated by a highly dilute solution of carmine. Such a solution serves, therefore, as a standard. M. J. S.

**Apparatus for Estimating Sulphur in Coal-Gas.** By FERDINAND FISCHER (*Zeit. angw. Chem.*, 1897, 302—303).—Fifty litres of the gas are burned from a bunsen burner, and the products of combustion passed through an apparatus consisting of a tube provided with six bulbs, inclosed in a larger tube through which a current of cold water flows. The liquid condensed in the bulb tube runs out through a narrow tube at the lower part of the apparatus, where it is collected in a flask. Sufficient hydrogen peroxide is added to the condensed liquid to oxidise the sulphurous acid, and the sulphuric acid is titrated by means of N/10 alkali, or estimated gravimetrically.

The apparatus may also be used for estimating sulphur in petroleum. L. DE K.

**Microchemical Reaction for Nitric Acid.** By J. L. C. SCHROEDER VAN DER KOLK (*Jahrb. f. Min.*, 1897, i, 219).—The following test, which is somewhat similar to that proposed by Brauns (this vol., ii, 343), has been used by the author for several years. The substance to be tested is placed with a drop of sulphuric acid in the hollow in a glass slide, and from the cover-glass hangs a drop of barium hydroxide solution; when nitric acid is driven off, typical crystals of barium nitrate appear in the drop on the cover-glass. As the substance tested does not come in contact with the barium solution, the presence of sulphates, phosphates, &c., does not affect the result. L. J. S.

**Estimation of Hydrochloric Acid in the Gastric Juice.** By HERMANN STRAUSS (*Chem. Centr.*, 1896, i, 1024—1025; from *D. Arch. Klin. Med.*, **56**, 87—120).—Dimethylamidoazobenzene, recommended by Töpfer for this purpose (Abstr., 1894, ii, 262), is ten times as sensitive as Congo red paper for the detection of free hydrochloric acid, but owing to the somewhat wide limits of the change from red

to yellow, the recognition of the neutral point is influenced by the differently developed sense of colour estimation in individuals. A 1 per cent. aqueous solution of Congo red is still more sensitive, and is best used by testing drops removed from the liquid under titration (Töpfer method), taking as the neutral point that at which a bluish-black colour is no longer observed in the contact zone of the two drops. Acid phosphate solutions, with both these indicators, produce changes which may be mistaken for those caused by highly dilute acids, as do also organic acids, especially lactic acid, when present in such proportions as occur in pathological human gastric juice. Töpfer's method of estimating the loosely combined hydrochloric acid with alizarin demands a highly developed power of recognising colour changes. In any case, a quantitative comparison of the amount of free hydrochloric acid with the total acidity affords a better means of judging whether the composition of the secretion exceeds the normal limits than a mere estimation of the total acidity with the qualitative detection of free hydrochloric acid. M. J. S.

**Detection of Traces of Fluorine in Beer.** By Wilhelm Windisch (*Chem. Centr.*, 1896, ii, 60; from *Wchschr. Brauerei*, 13, 449).—A litre of the beer (more or less according to the proportion of fluorine) is deprived of carbonic anhydride, filtered, heated to boiling, and mixed with 400 c.c. of hot lime-water. The clarified upper liquor is drawn off, and the precipitate collected on a linen filter, dried as far as possible by wrapping in the linen and pressing between filter paper, transferred to a platinum crucible, dried, and ignited. It is then pulverised in the crucible, moistened with 3 drops of water, and 1 c.c. of concentrated sulphuric acid added, the escaping gas being allowed to act on a large watch glass which has been coated with wax and etched through in the usual manner; the watch glass is cooled by ice-cold water. It is admitted that the whole of the fluorine is not contained in the precipitate, but that a further amount can be thrown down by a second treatment with lime water. M. J. S.

**Detection of Soda or Borax in Milk.** By P. Solomin (*Chem. Centr.*, 1896, ii, 66; from *Hyg. Rundsch*, 6, 445, *Hyg. Inst. Berlin*).—The author has tested a method suggested by Tscherbakoff, which consists in simply mixing the milk with an equal volume of 95 per cent. alcohol. Normal milk yields a coarse clot in, at most, half-a-minute. The clotting is delayed for 5 minutes by the presence of 0·06 per cent. of soda (Tscherbakoff says 0·02) and the clot is then a finely divided one. In milk 24 hours old, 0·1 per cent. of soda is required to hinder the coagulation, and 0·2 per cent. after 48 hours. Borax behaves similarly; 0·08—0·1 per cent. being the minimum that can be detected. M. J. S.

**Rapid Method for the Estimation of Boric Acid in Milk.** By Georges Denigès (*J. Pharm.*, 1897, [vi], 6, 49—54).—Although, according to Farrington (this vol., ii, 194), a solution of boric acid in milk shows a greater acidity than when the same amount of acid is dissolved in water, yet the author finds that, for solutions containing 1, 2, or 3 grams of boric acid per litre, the solutions in milk do not

exhibit so great an acidity as do corresponding solutions in water mixed with glycerol. The greater acidity in milk is due to milk-sugar. The method recommended is as follows. Twenty c.c. of milk is placed in each of two flasks, to one of which 2 or 3 drops of phenolphthalein and sufficient N/10 sodium hydroxide to cause a permanent pink tint are added; 10 c.c. of a mixture of equal volumes of ethylic alcohol (90°) and glycerol is then added, and subsequently sufficient N/10 sodium hydroxide to bring back the pink colour which had disappeared. If $n$ = the number of c.c. of N/10 alkali required in the second case, then $n - 0{\cdot}15$ gives in grams the amount of boric acid in 1 litre of milk. The amount is correct to 1 or 2 decigrams. If the milk contains more than 3 grams of boric acid per litre, it is necessary to dilute before taking the 20 c.c. The method is only accurate when the amount of boric acid is below 3 grams per litre and the amount of milk-sugar is between 40 and 50 grams per litre. J. J. S.

**Estimation of Sodium in Presence of Potassium.** By Feodor F. Beilstein and O. von Blaese (*Zeit. anal. Chem.*, 1897, **36**, 513; from *Bull. Acad. Sci. de St. Pétersbourg*, **33**, 209).—To the solution of the chlorides or nitrates, a solution of potassium antimonate is added. The supernatant liquid is decanted after 24 hours and the precipitate washed, first with a 0·7 per cent. solution of potassium acetate, and then with 50 per cent. alcohol. After ignition, it is weighed as $NaSbO_3$. For each 100 c.c. of the decanted liquid (which must not contain potassium carbonate), 0·0233 gram must be added to correct for solubility. M. J. S.

**Estimation of Alumina in Phosphates.** By Henri Lasne (*Zeit. angw. Chem.*, 1897, 276—278; reply by von Grueber (*Zeit. angw. Chem.*, 1897, 278).—The first author (this vol., ii, 191) claims priority for the use of sodium hydroxide in the separation of aluminium phosphate from iron and the earthy phosphates (Abstr., 1892, ii, 233), and states that the few alterations proposed by von Grueber cannot be considered as improvements, but rather the reverse. In reply, the latter states that he was unacquainted with Lasne's investigation.

L. de K.

**New and Rapid Method for the Qualitative Separation of Iron, Aluminium, Chromium, Manganese, Zinc, Nickel and Cobalt.** By Alexander R. Cushman (*Amer. Chem. J.*, 1897, **19**, 606—607).—Precipitate with ammonium chloride, ammonia, and ammonium sulphide. Warm the well washed precipitate with moderately dilute hydrochloric acid in a porcelain dish; complete solution indicates the absence of nickel and cobalt, but if a black residue remains, this is dissolved by adding aqua regia. The excess of acid and chlorine is then expelled by evaporation, the solution made strongly alkaline with ammonia (after previously adding ammonium chloride in case the amount of hydrochloric acid used on the sulphides was small), bromine solution is added in excess, the whole allowed to remain a few minutes and filtered, giving precipitate (1) and filtrate (1).

The *precipitate* (1), removed from the filter, is treated with potassium hydroxide in excess and with bromine solution, and filtered, the *filtrate*

being (2). A portion of the *residue* is dissolved in hydrochloric acid and tested for iron with thiocyanate; another portion is tested for manganese by fusion with sodium carbonate and nitrate. A portion of the filtrate (2) is acidified with hydrochloric acid, treated with excess of ammonium carbonate, and boiled, to see if aluminium is present; another portion is tested for chromium with acetic acid and lead acetate.

To the original *filtrate* (1), a large excess of potassium hydroxide is added, and the whole filtered after a few minutes. The greenish-white *precipitate* (2) is nickel, and is confirmed by the blow-pipe test with a bead of microcosmic salt. The *filtrate* (3) from this is boiled, when cobalt is precipitated, and is confirmed by the borax bead, whilst the filtered solution (4) is tested for zinc by acidifying with acetic acid and saturating with hydrogen sulphide, the presence of the metal being confirmed by igniting the precipitate with cobalt nitrate on charcoal.

C. F. B.

**Estimation of Carbon in Iron.** By LEOPOLD SCHNEIDER (*Chem. Centr.*, 1896, i, 1026; from *Oesterr. Zeit. Berg-Hütt.*, **10**, 121).—The author has improved his process (Abstr., 1895, ii, 531) by substituting phosphor-copper for the copper powder. Phosphor-copper, containing 15 per cent. of phosphorus, is easily powdered, and burns in oxygen more readily than pure copper. It should be freed from iron by digesting for 24 hours with concentrated hydrochloric acid and washing with water, and a blank combustion with 10 grams should be made to prove the absence of carbon. In other respects, the process is not altered.

M. J. S.

**[Analysis of Ilvaite.]** By K. H. SCHNERR (*Jahrb. f. Min.*, 1897, i, 432 Ref.; from *Inaug.-Diss. München*, 1894). See this vol., ii, p. 507.

**Estimation of Manganese in Presence of Phosphoric Acid.** By GEORGES VIARD (*Bull. Soc. Chim.*, 1896, [iii], **15**, 973—975).—The method for the estimation of manganese proposed independently by Hannay, and by Beilstein and Jawein consists in adding potassium chlorate in successive small quantities to the manganese solution, strongly acidified with nitric acid and heated to boiling, the precipitated peroxide being collected, ignited, and weighed. The author calls attention to the fact that this method is inapplicable in presence of phosphoric acid, owing to the precipitation of trimanganic phosphate under the conditions of the experiment.

A. C. C.

**Volumetric Estimation of Zinc.** By K. DEMENTÉEFF (*Chem. Centr.*, 1896, ii, 207; from *Pharm. Zeit. Russ.*, **35**, 263).—The zinc compound, which must be free from heavy metals, is dissolved in soda, and in a portion of the solution the total bases are titrated by acid, using as indicator tropæolin, which gives a yellow colour with alkali, and orange-red with acid. In another portion, the soda alone is titrated with phenolphthalein, and the zinc is calculated from the difference between the two titrations.

M. J. S.

**Quantitative Analysis by Electrolysis.** By E. WAGNER (*Chem. Centr.*, 1896, ii, 58—59; from *Zeit. Elektrotech. und Elektrochem.*, **2**,

613—616).—*Copper.*—In a platinum basin of 100 square cm. effective surface, with an anode of perforated platinum foil 45 mm. in diameter, 1 gram of $CuSO_4$ can be electrolysed; for this purpose, the copper solution is added to a solution of 4 grams of ammonium oxalate in 60 c.c. of water, the temperature is raised to 60°, and the solution electrolysed for 30 minutes with a current of 0·05 ampère; 5 c.c. of cold saturated solution of oxalic acid is then added, the current increased to 0·5 ampère, and during the next 80 minutes 5 c.c. of oxalic acid is added four times. Deposition is complete in 2 hours. The copper is washed with water and alcohol as usual, and dried for 5 minutes at 100°. *Zinc.*—The solution containing 1·5—1·8 gram of $ZnSO_4$ in 40 c.c. of water is gradually added to one of 4 grams of ammonium oxalate in 60 c.c. The solution is heated to 55—60°, and electrolysed with 0·2 ampère; 15 minutes later, 5 c.c. of 6 per cent. tartaric acid solution is added, taking care not to pour it on the anode, and during the next 2 hours this addition is 5 times repeated, whilst the current is augmented to 0·4—0·5 ampère, with an electromotive force of 3—3·2 volts. The deposition is complete in 2—2½ hours. The zinc is washed and dried like the copper, but at 70°. M. J. S.

**Employment of Cupric Salts in the Analysis of Irons and Steels.** By ADOLPHE CARNOT and GOUTAL (*Compt. rend.*, 1897, **125**, 75—80).—*Carbon.*—The ordinary operation of dissolving iron or steel in cupric chloride for the estimation of carbon can be greatly accelerated, without any risk of loss of carbon, by placing in the bottom of the flask used a perforated disc of platinum about 11 cm. in diameter, and employing, for each gram of metal taken, 50 c.c. of a 30 per cent. solution of cupric potassium chloride and 4 or 5 drops of hydrochloric acid. A current of carbonic anhydride is passed into the liquid, so that the upper part of the flask is continually filled with this gas. The copper solution is first placed in the flask, heated to boiling for a few minutes, cooled to 60°, and the iron or steel added, the whole being afterwards heated at 90—95°. Fine filings are dissolved in 20 minutes, and even lumps of 5 grams are dissolved in an hour and a half. The residue is treated in the usual way, and should be burnt in oxygen without being previously dried.

*Sulphur.*—When iron or steel is dissolved in very slightly acidified cupric potassium chloride solution under the conditions specified, all the sulphur remains in the insoluble residue, which is well washed and treated with a mixture of 5 c.c. of hydrochloric acid, 15 c.c. of water, and 1 c.c. of bromine for some time in the cold, then slowly heated, and finally boiled. The liquid is neutralised with ammonia, re-acidified with a small quantity of hydrochloric acid, and the sulphuric acid precipitated with barium chloride. The whole estimation can be completed in 3 hours.

*Phosphorus.*—If the cupric potassium chloride solution is quite neutral, all the phosphorus remains in the residue, which is treated with nitric acid and bromine, filtered, boiled with some chromic acid to oxidise hydrocarbons, neutralised with ammonia, reacidified with nitric acid, and precipitated with ammonium molybdate. The precipitate has its normal composition. Any arsenic present is dissolved by the copper solution.

*Chromium.*—With a neutral copper solution, the chromium remains in the residue, which can be heated with sodium peroxide, the chromic acid being estimated in an aqueous solution of the fused mass.

*Tungsten and Titanium.*—The residue left by the neutral copper solution is treated with hydrofluoric acid to remove silica, and then fused with a mixture of 4 parts of potassium nitrate and 1 part of potassium carbonate. The product is treated with water, and the tungsten estimated in the solution by means of mercurous nitrate (Defacqz, this vol., ii, 163). The residue containing the titanium is fused with potassium hydrogen sulphate, dissolved in water, and mixed with sulphurous acid to reduce the ferric sulphate; sodium acetate is then added, the liquid boiled, and the titanium oxide collected and weighed.

When there is doubt as to the nature of the precipitate, it is heated with a small quantity of potassium hydrogen sulphate and a few drops of sulphuric acid. After cooling, a crystal of quinol is added; titanium gives a carmine-red coloration (Lévy), whilst tungsten gives an amethyst-violet coloration (Defacqz).

To detect traces of tungstic acid, the residue left by the copper solution is washed, treated with hot concentrated ammonia, and the liquid evaporated to dryness. The residue is treated in the manner just described. C. H. B.

**Electrolytic Analysis of Bronze and Brass.** By A. Hollard (*Compt. rend.*, 1897, **124**, 1451—1453).—Five grams of the bronze or brass is dissolved in a mixture of 25 c.c. of nitric acid of 36° B. and 15 c.c. of concentrated sulphuric acid, and the liquid is diluted to 350 c.c. and heated nearly to its boiling point until any undissolved stannic oxide readily agglomerates and settles to the bottom of the vessel. The estimation of the copper is conducted in the manner previously described (this vol., ii, 161), and the residual liquid is evaporated nearly to dryness. The tin is precipitated as sulphide, washed, dissolved in ammonium sulphide, the solution evaporated to dryness, and the residue treated with potassium chlorate and excess of hydrochloric acid. The solution thus obtained is evaporated to dryness, dissolved in 30 c.c. of hydrochloric acid diluted with water, 30 grams of pure ammonium oxalate added, and the tin precipitated with a current of 0·7 ampère, the liquid being kept at a temperature of about 90°, and the electrodes being slightly roughened. The roughening is effected by depositing zinc on the electrodes, removing it by means of nitric acid, and afterwards immersing the electrodes in fused potassium hydrogen sulphate, the whole process being repeated if necessary.

The liquid from which the copper and tin have been precipitated is heated to expel hydrogen sulphide, evaporated almost to dryness, dissolved in water, neutralised with ammonia, mixed with 15 c.c. of a 10 per cent. ammonium citrate solution, 13·8 gram of ammonium acetate (or 9·4 c.c. of glacial acetic acid neutralised with ammonia), and 3 c.c. of glacial acetic acid; on submitting the solution to the action of a current of 0·6 ampère for about 12 hours, all the zinc is precipitated. Iron, if present, is partially precipitated with the zinc, but the amount is readily estimated by means of permanganate. Lead, if present, is precipitated as peroxide (*loc. cit.*). C. H. B.

**Electrolytic Estimation of Lead.** By O. VON GIESE (*Chem. Centr.*, 1896, i, 1209, 1284—1285; from *Zeit. Elektrotech. u. Elektrochem.* 2, 586—588. See Abstr., 1894, 161, 217, 480; 1895, ii, 418).—The author has revised the work of Kriechgauer on this subject. Whilst the deposition of lead as dioxide from a solution of the nitrate is favoured by the rise of temperature, this should not exceed 60°, since, at 70°, the deposition is incomplete in consequence of the decomposition of nitric acid. Between 50° and 60°, the time of deposition varies directly with the amount of lead present, and inversely with the area of the electrodes. At this temperature, a current of 0·5—1 ampère gives the best yield, and the deposits are dense, adhere well to the basin, and can be dried completely at 80—100°. Electrodes with a matt surface are recommended. Increase of potential shortens the time of deposition more than increase of current; about 0·95 volt. being the minimum. To prevent precipitation of lead on the cathode, 15 per cent. of nitric acid must be added to a 2·5 per cent. solution of lead nitrate, 17·5 per cent. of acid to a 3·75 per cent. solution of lead salt, and 20 per cent. of acid to a 5 per cent. solution. On a capsule with 180 square centimetres of surface, 5·5 grams of lead dioxide can be deposited. M. J. S.

**New Reactions of Vanadic Acid, Molybdic Acid, and Thiocyanates.** By W. ELLRAM (*Chem. Centr.*, 1896, ii, 211, 212; from *Sitzungsber Naturforsch. Ges. Univ. Dorpat*, 1895, 28).—A solution of potassium thiocyanate (1 : 12,000) treated with a vanadate and a trace of sulphuric acid, becomes yellow; with a little more acid, blue. Thiocyanates can thus be detected in saliva, serum, and milk (after removing albumin, &c., from the two latter by zinc sulphate). Similarly, vanadic acid, at a dilution of 1 : 5000, can be detected by thiocyanate. Molybdic acid similarly treated gives yellow, orange, and blood-red colorations. Even at a dilution of 1 : 1,000,000, a rose colour is perceptible. M. J. S.

**Estimation of Gold and Silver in Auriferous Minerals.** By P. TRUCHOT (*J. Pharm.*, 1897, [vi], 5, 493—495; from *Ann. Chim. analyt.*).—The mineral is finely ground so as to pass through a No. 80 sieve, and 100—200 grams of the powder is then roasted in a muffle so as to destroy pyrites, arsenides, tellurides, &c., stirring from time to time. The roasted mineral is then transferred to a flask, covered with saturated bromine water, and digested for 36 hours, fresh bromine water being added if the liquid becomes colourless. The solution is now filtered, the residue well washed, and the filtrate and washings, after acidification with hydrochloric acid, are evaporated in a porcelain basin to about 200 c.c. If necessary, the solution is again filtered, and the gold is then precipitated by a solution of ferrous sulphate acidified with sulphuric acid. The residue obtained above, after treatment with bromine water, contains the silver in the form of silver bromide; this can be dissolved out by concentrated ammonium chloride, and then precipitated in the usual way as silver bromide. J. J. S.

**Destruction of Organic Matter in Toxicology.** By ANTOINE VILLIERS (*Compt. rend.*, 1897, 124, 1457—1458).—The matter is

mixed with hydrochloric acid diluted with 2 or 3 times its volume of water, or less in special cases, and a few drops of a solution of manganese and a small quantity of nitric acid are added; the flask is then carefully heated, fresh quantities of nitric acid being added from time to time. The gases evolved consist of almost pure carbonic anhydride and nitrogen, and decomposition proceeds regularly without any formation of obnoxious volatile products. All the softer organs are very rapidly destroyed, but muscular fibre requires about an hour. The only substance that remains unoxidised is fat, which seems to be partially converted into substitution products. C. H. B.

**Estimation of Dry Matter in Peat.** By HEINRICH C. TRYLLER (*Landw. Versuchs-Stat.*, 1897, **49**, 145—161).—A number of estimations of dry matter in peat are given. The figures show that, for most purposes, sufficiently concordant results are obtained by heating at 105°, and allowing it to cool over sulphuric acid. The very divergent results obtained by Puchner (Abstr., 1895, ii, 544) could not have been due either to oxidation or to absorption of acid vapours from ordinary sulphuric acid as suggested.

A modified form of L. Meyer's air-bath was used in the experiments, and is described, with sketch. N. H. J. M.

**Estimation of Paraffin.** By HERMANN EISENLOHR (*Zeit. angw. Chem.*, 1897, 300—302; 332—336).—The author has proved, by a large number of experiments, that the methods now in use for the estimation of paraffin, are only fit for the assay of hard paraffins; they utterly fail when testing soft paraffins. The following process is recommended when dealing with a brown-coal product containing not more than 14 per cent. of oily matter, and melting between 31·5° and 60°. 0·5 gram of the sample is dissolved in 100 c.c. of absolute alcohol; 25 c.c. of water is slowly added, stirring, meanwhile, with a thermometer, and the vessel is placed in a freezing mixture made of equal parts of ice and salt, so as to cool the mixture to −18 or −20°. After a short time, the paraffin has quantitatively separated, and is then collected on a filter previously dried at 35°; the funnel is, of course, placed in an apparatus, the temperature of which does not exceed −18°. The precipitate is washed with alcohol of the same strength, until the filtrate no longer becomes turbid on adding water; the filter and contents are then dried to constant weight in a vacuum at 35—40°; this generally takes from 6 to 8 hours. L. DE K.

**Detection of "Rosin Oil" in Turpentine.** By A. AIGNAN (*Compt. rend.*, 1897, **124**, 1367—1368).—The method previously described (Abstr., 1890, 422) is not applicable when the proportion of "rosin oil" is below 2 per cent. When pure turpentine is distilled, the rotatory power of the successive fractions diminishes, and the same phenomenon is observed with turpentine mixed with rosin oil, but in the latter case the residue left in the retort has a much lower rotatory power than the corresponding residue from the pure substance. For example, the residue of 70 c.c. from 250 c.c. of pure turpentine, had a rotatory power of −51·5°; the corresponding residue from turpentine adulterated with 3 per cent. of rosin oil, had a rotatory

power of only $-36 \cdot 21°$, whilst with 5 per cent. of rosin oil, the rotatory power was only $-28 \cdot 6°$.

When $n$ per cent. of rosin oil is introduced into turpentine, the rotatory power of a similar residue, in a column 200 mm. long, is reduced by *at least* $n \times 5° 30'$. Further, by distilling at 100° under a pressure of 60 mm., it is possible to obtain a *dextrogyrate* residue from a turpentine containing only 0·5 per cent. of rosin oil.

C. H. B.

**Estimation of Chloroform in Viscera.** By Bernhard Fischer (*Zeit. anal. Chem.*, 1897, **36**, 549; from *Jahresb. chem. Untersuchungsamts der Staadt Breslau*, April, 1894, to March, 1895).—After the viscera have been distilled with water until all the chloroform has passed over, the distillate is mixed with potassium carbonate, warmed to 60°, and washed air aspirated, first through the liquid, then through a combustion tube heated to bright redness, and finally through a solution of silver nitrate. In chloroform poisoning, the chloroform is found chiefly in the blood and brain. In all cases, its presence must be confirmed by the isonitrile reaction.

M. J. S.

**Examination of Chloroform.** By Auguste Béhal and Maurice François (*J. Pharm.*, 1897, [vi], **5**, 417—424).—It is well known that pure chloroform cannot be kept for any length of time, as it decomposes in contact with air and in presence of sunlight, evolving carbonyl chloride; the admixture of a little alcohol, however, prevents the decomposition taking place. The author has examined a number of specimens of chloroform, and finds that the only impurities are water and alcohol. The water causes the chloroform to partially solidify when cooled to between $-20°$ and $-40°$. An accurate method of estimating the amount of alcohol present is described; for this purpose, the chloroform is shaken with strong sulphuric acid, and the alcohol is thus removed in the form of ethyl hydrogen sulphate; when the acid extract is boiled with water, this is decomposed, and the alcohol can be distilled off and estimated by oxidation to acetic acid. J. J. S.

**Estimation of Maltose in Worts.** By Ludwig Braun (*Chem. Centr.*, 1896, ii, 67—68; from *Zeit. ges. Brauw.*, **19**, 241, 254).—The conventional method laid down in 1890 by the Vienna Conference is in many respects incomplete. Experiments show that the estimation should take place as soon as possible after the clarifying of the wort. The choice of vessels is important. The conference prescribed capsules of 13 cm. diameter; the use of capsules 9 cm. diameter, which give the same results, is general, but they should always be covered when in use. Shallower basins give lower results. Glass vessels do not give the same results as those of porcelain, either from their different heat conductivity, or from the difference in the surface exposed. In accordance with the Vienna instructions, the Fehling's solution should first be heated to boiling, then the wort added, and the boiling continued for 4 minutes. Filtration should take place immediately, without the addition of the 50 c.c. of cold water prescribed by Kusserow, which leads to lower numbers. Kjeldahl's method (Abstr., 1896, ii, 580) gives widely different results, mainly in consequence of the longer

heating, and the author gives the preference to the Vienna method, if the above precautions are observed. M. J. S.

**Estimation of Milk-Sugar in Milk.** By HENRY DROOP RICHMOND and L. KIDGELL BOSELEY (*Analyst*, **22**, 1897, 98—100).—The authors have recalculated the figures on the strength of which Wiley and Ewell (Abstr., 1896, ii, 628) recommended their process for the estimation of lactose in milk, and have found them to be erroneous, so that the experimental error is about twice as great as those chemists supposed.

A slight modification of Vieth's process is described; this consists in clarifying the sample with mercuric nitrate and then making a correction for the volume of the deposit. To 100 c.c. of milk, 3 c.c. of acid mercuric nitrate is added to compensate for the volume of the proteids; as much water as corresponds with the fat multiplied by 1·11; then, again, as much water as corresponds with one-tenth of the degrees of specific gravity, and also a sufficient volume of water to reduce scale readings to percentages of milk-sugar. So if a milk contain 3·7 per cent. of fat and has a specific gravity of 1·0325, then $3 + 4{\cdot}1 + 3{\cdot}25 + 10$ (if a Mitscherlich half-shadow polariscope is used) $= 20{\cdot}35$ c.c. must be added to 100 c.c. of the sample. In this way, calculation is dispensed with. L. DE K.

**Estimation of Starch in Cereals.** By LÉON LINDET (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1163—1164).—The grain, about 10 grams in weight, after being bruised, is transferred to a conical flask, covered with a solution containing 1·5 per cent. of hydrogen chloride and 2 per cent. of pepsin, and the whole kept for 12—24 hours at 40—50°. The pepsin serves to destroy the gluten, which forms a network round the starch granules, and the hydrochloric acid prevents the action of the diastase on the starch. The flask is occasionally shaken, and the contents are then poured on to a piece of silk such as is used for dressing flour (No. 80—100), the silk is folded and then kneaded several times with fresh quantities of water until no more starch escapes from the silk. The combined amylaceous liquids are mixed with a little formaldehyde or mercuric chloride and then poured on to a tared filter. The filtration is tedious, and may be hastened by the addition of a weighed quantity of washed and calcined pumice. J. J. S.

**Estimation of Starch in Sausage Meat.** By JOSEPH MAYRHOFER (*Chem. Centr.*, 1896, ii, 70; from *Forsch.-Ber. Lebens und ihre Bez. z. Hyg.*, **3**, 141).—A quantitative estimation is necessitated by the fact that, in some German districts, the addition of 2—3 per cent. of farina is officially permitted. The author makes use of the fact established by Dragendorf, that starch is insoluble in alcoholic potash, whilst sugar, fat, albumin, &c., are dissolved. For this purpose, 60 grams of the sample is digested on the water bath with an 8 per cent. alcoholic potash solution. In the absence of starch, everything will dissolve except cellulose. The solution is diluted with hot alcohol, and the insoluble matter collected on a filter and washed with alcohol until free from alkali. It is then dissolved in aqueous potash, and the solution acidified with acetic acid. The starch is precipitated by the addition of alcohol, collected, washed, dried, and weighed. M. J. S.

**Distinctive Reaction for α- and β-Naphthol.** By Eugène Leger (*J. Pharm.*, 1897, [vi], **5**, 527—529).—A solution of sodium hypobromite is made by diluting 30 c.c. of sodium hydroxide solution (36° B.) with 100 c.c. of water, then adding 5 c.c. of bromine and shaking vigorously. Two drops of the above solution are added to 10 c.c. of a saturated aqueous solution of α- or β-naphthol, obtained by triturating the solid naphthol for some few minutes with water. In the case of the α-compound a dirty violet coloration, and even a precipitate, is formed; the reaction is very sensitive, and occurs when the naphthol solution is diluted with 9 volumes of water. In the case of β-naphthol, a yellow coloration is developed; this gradually becomes greenish and then again yellow. If the solution of the β-compound is diluted with its own volume of water, and treated in exactly the same way as described above, a yellow coloration is formed, but it disappears on shaking. By means of this test, 1 part of α-naphthol can readily be detected in 100 parts of β-naphthol. In making the tests, freshly prepared solutions must be used. J. J. S.

**Schiff's Reaction with "Acid Magenta."** By Leon Lefèvre (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1169—1171. Compare Cazeneuve, Abstr., 1896, ii, 630).—The author points out that the only difference in Schiff's reaction when using "acid magenta" instead of rosaniline hydrochloride itself is that the violet colour takes a slightly longer time to develop. J. J. S.

**Distillation of Formaldehyde from Aqueous Solutions.** By Norman Leonard, Harry M. Smith, and Henry Droop Richmond (*Analyst*, 1897, **22**, 92).—When distilling a solution of formaldehyde, the amount of the latter found in any fraction is expressed by the formula, $100 - y = \frac{(100 - x)^{1\cdot 65}}{100^{0\cdot 65}}$, in which $y$ represents the percentage of formaldehyde in the distillate and $x$ the volume of the fraction expressed as percentage.

Several analyses are given to prove the correctness of the formula, and also a table of the rates of distillation of formaldehyde, and of formic, acetic, propionic, and butyric acids. L. de K.

**Estimation of Aldehyde in Ether.** By Maurice François (*J. Pharm.*, 1897, [vi], **5**, 521—525).—The author makes use of the following solution. Water recently saturated with sulphurous anhydride 220 c.c., magenta solution (1 in 1000) 30 c.c., and sulphuric acid (66°) 3 c.c. A mixture of 5 c.c. of pure ether, 5 c.c. of 95 per cent. pure alcohol, and 4 c.c. of the above solution remains colourless for 15 minutes; if the ether contains more than 1/10000 part of aldehyde, the mixture assumes a reddish-violet colour, the intensity of the colour depending on the amount of aldehyde present. The amount of aldehyde in the ether is readily determined by comparing the intensity of the colour produced by it with that produced by 5 c.c. of alcohol containing 1/1000 or 1/10000 part of pure aldehyde, mixed with an equal volume of pure ether. J. J. S.

**Estimation of Benzaldehyde in "Kirschwasser."** By L. Cuniasse and Sig. de Raczkowski (*Zeit. anal. Chem.*, 1897, **36**, 403; from *Mon.*

*sci.*, [iv], 8, II, 915).—Two hundred c.c. of Kirschwasser is distilled as completely as possible, and the distillate made up to the original volume; 3—4 c.c. of a freshly-prepared solution containing 2 grams of phenylhydrazine hydrochloride and 3 grams of crystallised sodium acetate in 20 c.c. is added, and then water to make it up to 400 c.c. The precipitated benzylidenephenylhydrazine is collected, washed with very dilute alcohol, and dissolved in 10 c.c. of absolute alcohol; the alcoholic solution is then evaporated in a vacuum, and the residue weighed. One part corresponds with 0·54 part of benzaldehyde. M. J. S.

**Recognition of Certain Organic Acids in Plants.** By ARMAND BERG and C. GERBER (*Bull. Soc. Chim.*, 1897, [iii], **15**, 1050—1055. Compare Abstr., 1895, ii, 297).—Citric acid may be detected in presence of oxalic, tartaric, and malic acids in the following manner. The dry substance is heated with 5—6 parts of sulphuric acid (66° B.) during $1\frac{1}{2}$ hour at 50—60°, cautiously diluted with water (5 vols.), and extracted with ether, which is then removed, and evaporated in two separate portions. One part of the residue is dissolved in water and treated with a dilute solution of ferric chloride, which develops a reddish-violet coloration; the remainder is treated with a dilute, freshly-prepared solution of sodium nitroprusside, and subsequently with a drop of concentrated soda, when an intense red coloration is produced. These colour changes depend on the conversion of citric into acetonedicarboxylic acid under the influence of sulphuric acid.

Although the test already described (*loc. cit.*) is applicable to citric, tartaric, and malic acids, the last-named may be distinguished in presence of the other two on account of the solubility of the ammonium salt in alcohol; if ammonia is passed into an alcoholic solution of the acids, the residue obtained on evaporating the filtrate gives the indication in question only when malic acid is present.

The authors describe their scheme for recognising organic acids in plants, based on these additions to existing methods. M. O. F.

**Simple Method of Estimating Fat in Centrifugalised Cream.** By MATS. WEIBULL (*Bied. Centr.*, 1897, **26**, 491—492; from *Kongl. landtbr.-akad. handl. tidskr.*, 1896, 370—379).—The proposed method depends on the relation between the amounts of fat ($f$) and dry matter ($d$) contained in cream. This relation is expressed by the equation: $d = f + \frac{100 - f}{100} /$ constant. The constant being 8·7, $f = 1·1\,d - 9·5$.

The dry matter of the cream is determined by mixing about 6 grams with finely powdered pumice (20 c.c.) and heating for $2\frac{1}{2}$ hours at 100°.

A number of determinations were made by this method, most of which (71 per cent.) showed an error of less than 0·5 per cent. Only in one case did the error amount to 1 per cent. N. H. J. M.

**Cryoscopy applied to the Analysis of Milk.** By E. CARLINFANTI (*Gazzetta*, 1897, **27**, i, 460—466).—Using the Beckmann cryoscopic apparatus, the author shows that the freezing point of milk is $-0·55°$ to $-0·59°$; as the milk becomes changed by keeping,

its freezing point falls, but a milk freezing at $-0{\cdot}59°$ cannot be described as bad. The experiments show that the freezing point is quite independent of the proportion of fats or proteids present, but is determined by the quantity of material actually in solution; the addition of a 9 per cent. lactose solution, freezing at $-0{\cdot}55°$ to $-0{\cdot}59°$, to the milk does not alter its freezing point. The freezing point is, however, raised by $0{\cdot}05°$ to $0{\cdot}065°$ for each 10 per cent. of water added.

The cryoscopic method can thus be used to detect the adulteration of milk. W. J. P.

**Detection of Mixtures of Diluted, Condensed, or Sterilised Milk with Fresh Milk.** By HENRY DROOP RICHMOND and L. KIDGELL BOSELEY (*Analyst*, 1897, **22**, 95—97).—The authors base their process on the fact that sterilised, or diluted, unsweetened, condensed milk throws up its cream slowly and imperfectly; the albumin has also undergone alteration and the rotatory power is affected.

One hundred c.c. of the sample is put into a creamometer for 6 hours at 15·5° and the percentage of cream is read off. At least 2·5 per cent. of cream should rise for every 1 per cent. of fat in the milk; so if the amount of the cream falls below 2 per cent. for each 1 per cent. of fat, sterilised (or unsweetened condensed) milk is likely to be present.

The albumin is then estimated by the Sebelein and Duclaux method. If less than 0·35 per cent. is found, sterilised milk may be considered to be present. Further evidence may be obtained from the result of a polarimetric observation; if much sterilised milk is present, the amount of lactose thus found will be less than that obtained by a gravimetric experiment.

A fairly good quantitative approximation may be obtained by using the formula:

$$\text{Percentage of sterilised milk} = 100\frac{0{\cdot}4 - \text{per cent. soluble albumin}}{0{\cdot}4}$$

or from the cream rising test: $\text{Percentage of sterilised milk} = \dfrac{2{\cdot}5 - C/F}{2{\cdot}2}.$

L. DE K.

**Characterisation of Margarine by Admixture of Starch.** By FRANZ SOXHLET (*Bied.-Centr.*, 1897, **26**, 489—490; from *Milchzeit.*, 1897, No. 2, 17).—As regards the addition of starch to margarine instead of phenolphthalein, as recommended by the author, it is pointed out that whilst the limit of the iodine reaction is only reached when 1 gram is diluted with 50,000 parts of water, the reaction is much less delicate in presence of milk, when 1 gram of starch in 10,000 parts of milk can just be detected. To detect 20 per cent. of margarine in butter, the milk employed in the preparation of margarine would have to contain 7·5 grams of starch per litre, an amount which would be injurious to the keeping quality of the margarine. An objection raised against phenolphthalein is that it can be washed out. The same holds for starch, which can, moreover, be destroyed by the addition of malt extract. Raw starch would not have this disadvantage, but at least

1 per cent. would have to be added to margarine to show the iodine reaction.

The detection by means of raw starch is much more sensitive if the margarine is melted and the liquid underneath the fat treated with iodine; a reaction is then obtained with 2 grams of starch in 100 kilograms of margarine, or with butter containing 20 per cent. of margarine with 0·01 per cent. of starch. Raw starch, however, could not be employed with the margarine generally used in South Germany, as it does not dissolve in fat.

The detection of phenolphthalein is more simple than that of starch when the butter has to be first melted; and, finally, it is pointed out that genuine butter may easily come into contact with flour, and thus become liable to suspicion. N. H. J. M.

**Assay of Linseed Oil.** By WALTHER LIPPERT (*Zeit. angw. Chem.*, 1897, 306—307).—The paper is a criticism of Amsel's pamphlet on linseed oil and linseed oil varnish.

The author attaches great importance to the heating test. A good oil must remain clear even when heated to 300° and not give any flocculent deposit. The drying test depends, not only on the quality of the oil, but a good deal on the nature of the drier. A solution of manganous resinate in oil of turpentine containing a definite proportion of rosin and manganese might perhaps be found serviceable.

L. DE K.

**Detection of Arachis Meal and Arachis Cake in Chocolate.** By BILTERYST (*J. Pharm.*, 1897, [vi], 6, 29—30).—The examination may be made either microscopically or chemically. In the latter case, the fatty matter is extracted with carbon tetrachloride, and its refractive index determined in a Jean and Amagat's oleorefractometer. The index for cocoa fat is $-19°$, whilst for arachis it is $+3°$. A mixture containing 5 per cent. of arachis has an index $-18°$, and one containing 50 per cent. an index of $-7°$. This test can be supplemented by the determination of the proteids present, since chocolate contains 9, cocoa 18, arachis meal 20, and arachis cake about 45—47 per cent. of proteids. J. J. S.

**Detection of Japanese Wax and Tallow in Beeswax.** By L. S. LUGOWSKY (*J. Pharm.*, 1897, [vi], 5, 295—296; from *Pharm. Zeit. Russ.*, 1896, 35, 839).—The method commonly used is as follows: 50—60 grams of the suspected wax is distilled from a small retort, the distillate is washed with water and filtered, and the filtrate treated with a solution of lead acetate; the formation of a precipitate proves the presence of some fatty material in the original wax. The author, however, recommends the following process. The suspected sample is heated with a solution of borax saturated in the cold; if tallow is present, a white turbidity is produced, and if Japanese wax is present, a milky liquid. When cold, a layer of fat will be found under the layer of wax. The tallow and Japanese wax may be further identified by liberating the glycerol from them, and oxidising it to formic acid by means of potassium permanganate. J. J. S.

**Iodine Number of Cacao Butter.** By D. HOLDE (*Zeit. anal. Chem.*, 1897, 36, 381).—The maximum limit 51, given by De Negri and Fabris

in their monograph "Gli Olii," as also in the *Zeit. anal. Chem.*, 1894, **33**, 547 (Abstr., 1895, ii, 247), was quoted from the 1886 edition of Benedikt's *Analyse der Fette und Wachsarten*, p. 253, where it is erroneously given as Hübl's result. The number actually published by Hübl was 34. (See also Abstr., 1896, ii, 680). M. J. S.

**Detection of Tannin.** By BAEMES (*Zeit. anal. Chem.*, 1897, **36**, 518; from *Drug. Circ.*, **40**, 12, 308).—A solution is used containing 1 gram of sodium tungstate and 2 grams of sodium acetate in 10 c.c. In acid or alkaline solutions of tannin, this produces a straw-yellow precipitate insoluble in water. M. J. S.

**Estimation of Tannin.** By EUGEN AWENG (*J. Pharm.*, 1897, [vi], **5**, 294—295; from *Apoth. Zeit.*, 1896, 831).—Formaldehyde reacts with tannins, yielding insoluble condensation products known as tannoforms. The author has made experiments in order to determine whether this reaction could not be made use of in the estimation of tannin. The results in all cases come far too low, so that the method is altogether inapplicable. J. J. S.

**Adulteration of Sumach.** By MATTEO SPICA (*Gazzetta*, 1897, **27**, i, 349—358).—Silician sumach, especially when exported in the form of powder, is often largely adulterated with the leaves of a tamarisk (*Tamarix africana*), or of mastic (*Pistachia lentiscus*); the author gives various methods for detecting the fraud.

One method consists in determining the nitrogen by Kjeldahl's method; sumach leaves contain 0·9127 (0·87—0·98) per cent. of nitrogen, those of *T. africana* 1·7690 (1·48—1·99) per cent., and those of *P. lentiscus* 1·6345 (1·47—2·01) per cent.

The composition of the ash derived from the leaves of the various plants also affords a criterion of the purity of samples of sumach, and is given in the appended table.

| Ash. | Sumach. 6·60 | *T. africana.* 12·40 | *P. lentiscus.* 5·40 |
|---|---|---|---|
| | Composition of Ash. | | |
| Insoluble and $SiO_2$ | 24·05 | 37·10 | 6·20 |
| $CaO$ | 29·95 | 8·53 | 25·30 |
| $SO_3$ | 4·67 | 20·139 | 5·218 |
| $MgO$ | 6·25 | 9·368 | 5·760 |
| $Fe_2O_3, Al_2O_3$ | 7·15 | 7·400 | 7·410 |
| $CO_2$ | 12·60 | 1·130 | 13·750 |
| $P_2O_5$ | 3·344 | 1·1134 | 4·021 |
| $Cl_2$ | 3·101 | 4·4050 | 5·321 |
| $K_2O$ | 6·305 | 7·950 | 14·604 |
| $Na_2O$ | 2·004 | 2·630 | 12·176 |
| Total | 99·424 | 99·7654 | 99·760 |

Another method of detecting adulteration is afforded by applying Löwenthal's method for estimating tannin. The tannin is precipitated from the sumach extract as "copper tannate" by a cuprammonium solution; if the sumach is pure, this precipitate is completely soluble in dilute sulphuric acid, if adulterated with *T. africana*, a brick-red precipitate is left undissolved, and if sophisticated with *P. lentiscus*, a whitish precipitate remains undissolved by the dilute acid.

A colorimetric method of ascertaining the purity of sumach is also given, depending on the comparison of the colour of the extract with that of a standard solution containing 0·150 gram of safranine in a litre of water. Five grams of the sumach is boiled with 500 c.c., of water for half an hour, the liquid cooled, made up to 500 c.c. and filtered; to 25 c.c. of the filtrate, in a beaker, is added 5 c.c. of basic lead acetate solution (having the sp. gr. 1·184 at 15° and containing about 250 grams of basic lead acetate per litre) and 15 c.c. of caustic potash solution (having the sp. gr. 1·155 at 15° and containing 180 grams of potash per litre). The solution is then evaporated to 15 c.c., when, if it remains reddish-brown and practically clear, the sumach is pure; if the solution is yellow and contains any considerable amount of precipitate, foreign matter is present. The 15 c.c. of solution is now diluted to 250 c.c. and filtered; when examined in the Duboscq colorimeter, it should be of the same tint as the standard safranine solution.

Further, on warming sumach extract with much potash and a few drops of molybdate solution, a chocolate brown precipitate is obtained, which, if *T. africana* is present, is greenish by reflected light, and has a yellowish-brown reflex if sumach or mastic alone be present.

W. J. P.

**Estimation of Aloin in Aloes.** By G. L. SCHAEFER (*J. Pharm.*, 1897, [vi], **5**, 296; from *Pharm. Zeit.*, 1897, **42**, 95).—Fifty grams of aloes is dissolved in 300 c.c. of warm water to which a few drops of hydrochloric acid have been added; when cold, the solution is separated from the resin, 50 c.c. of ammonia (20 per cent.) and a solution of 15 grams of calcium chloride in 30 c.c. of water are added, and the whole rapidly shaken. At the end of 15 minutes, the precipitate is well pressed, or separated by means of a centrifugal machine. The precipitate is triturated in a mortar with hydrochloric acid, and the free aloin and calcium chloride dissolved in as little water as possible; the solution is filtered if necessary, and the residue washed with boiling water: the aloin separates from its aqueous solution on cooling. The best yields are obtained when ice is employed. J. J. S.

**Estimation of Theobromine in Cocoa and in Chocolate.** By L. MAUPY (*J. Pharm.*, 1897, [vi], **5**, 329—332).—Five grams of finely powdered cocoa are first extracted with light petroleum (60 grams) by boiling, and leaving the two in contact for a day; the dry residue is then triturated with 2 grams of distilled water, and the moist substance heated for an hour with 20 grams of 15 per cent. solution of phenol in chloroform; when cold, the mixture is filtered, and the residue twice boiled with 15 grams of chloroform. The chloroform is distilled from the united chloroform extracts, and the residue is heated for at least half an hour at 100°; when cold, 40 grams of ether (65° B.) are added,

and the mixture, after being well stirred, is put on one side for 6 hours; by this means, the theobromine is precipitated, whilst caffeine, colouring matters, and the last traces of fat go into solution. The mixture is then poured on to a weighed filter paper and washed with several c.c. of ether. In the case of chocolate, the residue, after extraction with light petroleum, is triturated with 4 c.c. of alcohol (70°) instead of with water. J. J. S.

**New Method for the Estimation of Casein in Milk.** By GEORGES DENIGÈS (*Bull. Soc. Chim.*, 1896, [iii], 15, 1116—1126).—The milk (25 c.c.) is placed in a 200 c.c. flask, 20 c.c. of a N/10 solution of mercuric potassium iodide and 2 c.c. of glacial acetic acid are added, and the whole is made up to 200 c.c. The mixture is then passed through a folded filter, the first few drops being rejected, and 12—15 c.c. of ammonia and 10 c.c. of potassium cyanide solution (equivalent to N/10 silver nitrate) are added to 100 c.c. of the filtrate; finally, decinormal silver nitrate is run in until a permanent precipitate is just formed. If $q =$ the number of 1/10 c.c. silver nitrate used, then the number of grams of casein per litre in the original milk can be found from the following table.

| $q - 48$. | Casein in grams per litre. | $q - 48$. | Casein in grams per litre. | $q - 48$. | Casein in grams per litre. | $q - 48$. | Casein in grams per litre. |
|---|---|---|---|---|---|---|---|
| 0......... | 0 | 12......... | 10 | 24......... | 22·25 | 36......... | 39 |
| 1......... | 1 | 13......... | 11 | 25......... | 23·5 | 37......... | 40·5 |
| 2......... | 1·75 | 14......... | 12 | 26......... | 24·75 | 38......... | 42·75 |
| 3......... | 2·50 | 15......... | 13 | 27......... | 26 | 39......... | 45 |
| 4......... | 3 | 16......... | 14 | 28......... | 27 | 40......... | 47 |
| 5......... | 3·75 | 17......... | 15 | 29......... | 28 | 41......... | 49 |
| 6......... | 4·5 | 18......... | 16 | 30......... | 29·25 | 42......... | 51·5 |
| 7......... | 5·5 | 19......... | 17 | 31......... | 30·75 | 43......... | 54 |
| 8......... | 6·5 | 20......... | 18 | 32......... | 32 | 44......... | 57·2 |
| 9......... | 7·15 | 21......... | 19 | 33......... | 33·5 | 45......... | 60 |
| 10......... | 8 | 22......... | 20 | 34......... | 35 | 46......... | 62·5 |
| 11......... | 9 | 23......... | 21 | 35......... | 37 | | |

J. J. S.

**Detection of Santonin in Urine.** By L. DACLIN (*J. Pharm.*, 1897, [vi], 5, 534).—The urine (30—40 c.c.) is treated first with lead acetate, and finally with crystallised sodium sulphate; after filtration, the limpid urine is gently evaporated in two porcelain dishes. After evaporation, 1 or 2 drops of sulphuric acid are added to the one dish, and the mixture gently warmed; the immediate appearance of a violet coloration indicates the presence of santonin. The residue in the second dish is treated with a few drops of alcoholic potash, when, if santonin is present a rose coloration is produced. The urine may also be extracted with chloroform, the chloroform evaporated, and the residue tested as above. Rhubarb gives neither of the above tests.

J. J. S.

# General and Physical Chemistry.

**Series Spectra of Oxygen, Sulphur, and Selenium.** By Carl Runge and Friedr. Paschen (*Ann. Phys. Chem.*, 1897, [ii], **61**, 641—686).—The authors have examined the compound line spectrum of oxygen, and give tables of the wave-lengths of the lines observed. In addition to the six triplets observed by Piazzi-Smyth, they find seven other triplets of similar character, these forming, with the other six, two distinct series. The differences between the rates of vibration of the three components of each triplet are, so far as this can be determined, the same. The thirteen triplets are distributed regularly over the spectrum, and the two series which they form are similar to those already observed with magnesium, calcium, strontium, zinc, cadmium, and mercury. There are, in addition to the triplet series, two other series of lines in the oxygen spectrum. These lines probably represent pairs, as the double character was distinctly observed in the case of four of the brightest.

Sulphur has a compound spectrum analogous to that of oxygen. Two series of triplets were observed, the first containing six and the second four. The differences in the rates of vibration of the three components are again about the same, and these differences are nearly five times greater than those obtained in the case of oxygen.

Selenium also has a compound spectrum, in which series of triplets appear; the appearances here are similar to those observed with oxygen and sulphur. H. C.

**Spectrum of Carbon.** By Arnaud de Gramont (*Compt. rend.*, 1897, **125**, 172—175 and 238—240).—When a condensed spark is allowed to play on fused alkali carbonates, the spectrum of the metal only is observed so long as the salt is in the flame, but if the flame is removed, the carbon lines appear, and their intensity increases with the difference of potential between the two sparking poles. A condensed spark on gas-carbon, purified by treatment with acids, shows the lines of many impurities, but Siberian graphite showed only a mixed band and line spectrum of carbon. The intensity of the bands increases in hydrogen, especially if the current of gas be rapid. On the other hand, the fused carbonates show only the carbon lines, and never the bands described by Swan. The method of experiment finally adopted by the author was to allow the condensed spark to impinge on the salt kept in fusion by passing an electric current through the platinum wire that supports the bead of salt, the whole being enclosed in a glass flask, through which hydrogen or any other gas can be passed.

The lines observed were 6578·5, 5662·2, 5648·6, 5641·0, 5379·9, 5151·6, 5144·6, 5132·9, 4267·0. In the case of the red doublet $C_{a}$, only the more refrangible component, at 6598·5, was observed, but the other line at 6584·0 was never observed even under widely varying conditions. The line 5695·1, described by Angström and Thalen, but

not photographed by Eder and Valenta, was seen rarely and irregularly, and seemed to be independent of the other lines. The author suggests that it may be an air-line. It was never observed with graphite in presence of hydrogen. The group 5662·2, 5648·6, and 5641·0 is readily, if faintly, visible, although it was not photographed by Eder and Valenta; on the other hand, the author was unable to observe the line 4556·3 of Eder and Valenta. The line $C_\beta$4267·0 is the strongest and most characteristic, and is the only line that has any value for analytical purposes; with a highly condensed spark, it broadens and becomes nebulous at the edges. The successive differences between the reciprocals of the wave-lengths show that the groups I and II are almost symmetrically arranged on either side of the intermediate line 5379·7.

Some of the cyanides, thiocyanates, and thiocarbonates show the same carbon spectrum as the carbonates. C. H. B.

**Some Emission Spectra of Cadmium, Zinc, and the Haloid Compounds of Mercury and some other Metals.** By A. C. Jones (*Ann. Phys. Chem.*, 1897, [ii], **62**, 30—53).—The emission spectra of cadmium and zinc, when the discharge is not a powerful one, consist of a number of bands built up of lines which decrease in intensity from the red to the violet end of the spectrum; these bands disappear when the discharge is a powerful one. The haloid compounds of mercury give a band spectrum, both in the visible and ultra-violet portions of the spectrum; in many cases, these bands consist of pairs of lines, but no numerical relationships could be established between them. Measurements of the wave-lengths are given. H. C.

**New Lines in the Spark Spectrum of Aluminium.** By Gustav A. Hemsalech (*Phil. Mag.*, 1897, [v], **44**, 289—291).—During the examination of the aluminium spectrum obtained by means of a coil giving a 10-inch spark, a number of lines were observed which were previously unrecorded. The wave-lengths were determined by a grating and 2 prisms, the means of the three values being, (1) 6828·2; (2) 6842·6; (3) 6928·2; (4) 7042·5; (5) 7057·9. Of these lines, (4) and (5) are the brightest, and (5) is probably double. L. M. J.

**Spectroscopic Investigation of the Blood.** By Louis Lewin (*Arch. Pharm.*, **235**, 245—255).—In these investigations, a Browning's pocket spectroscope was employed, a small glass bottle of about 2 c.c. capacity and having parallel sides being used to contain the specimen. The results of the experiments are shown in the form of a table giving the various absorption bands produced by oxyhæmoglobin, carboxyhæmoglobin, thiohæmoglobin, &c. J. F. T.

**Crystalline Form of Optically Active Substances.** By Hermann Traube (*Ber.*, 1897, **30**, 288. Compare this vol., ii, 2).—The author replies to Walden (*Ber.*, 1897, **30**, 98) and states that in all cases which have been completely examined, Pasteur's principle—that all optically active substances crystallise in non-superposably hemihedral forms—is found to hold. W. J. P.

**Connection between Volume Change and Specific Rotation of Active Solutions.** By Richard Přibram and Carl Glücksmann

(*Monatsh.*, 1897, **18**, 303—327).—The curve representing the relation between the percentage composition and the specific rotation of nicotine solutions may be regarded as built up of three different portions. The points of intersection would then lie at about 6 per cent. and 69 per cent. The addition of water to nicotine at first produces a very rapid fall in the rotation, but when the concentration of the nicotine reaches 69 per cent., the fall becomes less rapid, and from 6 per cent. onwards there is a rise in the rotation with increasing dilution. A solution containing about 69 per cent. of nicotine is the one that possesses the maximum density, and this point also coincides with the maximum volume contraction. The solution approximates to the composition $C_{10}H_{24}N_2 + 4H_2O$, and the authors are inclined to refer the peculiarities noticed in nicotine solutions to the existence of hydrates.

H. C.

**Production of Electricity by Chemical Means.** By ERNST ANDREAS (*Zeit. Elektrochem.*, 1896, **3**, 188).—The author has examined Borcher's cuprous chloride carbonic oxide cell, using carbon electrodes dipping respectively into solutions of cupric chloride in water, and of cuprous chloride in aqueous hydrochloric acid ; a porous diaphragm separated the two solutions, chlorine being passed into the cupric, and carbonic oxide into the cuprous solution. After a time, the current rapidly diminished, and it was found that the cuprous chloride was completely oxidised. The carbonic oxide had taken no part in the change ; of 1950 c.c. used in one experiment, 10 c.c. only were oxidised to carbonic anhydride. Similar results were obtained with electrodes of platinum, palladium, or nickel at various temperatures.

A gas battery consisting of two pieces of platinum gauze, separated by a sheet of filter paper moistened with the solution of an electrolyte, had a very low resistance, and gave encouraging results with coal gas and air, oxygen and hydrogen, or chlorine and hydrogen. The last combination, with the gases under a pressure of about 3 atmospheres, gave a current of about 1 ampère at 1·5 volts. Owing to the cost of the platinum, such a cell could not be a commercial success, but fairly good results were obtained by passing sulphurous anhydride on the one hand and chlorine on the other, under pressure, into carbon tubes dipping into dilute sulphuric acid. This combination gave 0·5 volt with 1 ohm resistance in circuit, and the products are sulphuric and hydrochloric acids. With large electrodes, good results would probably be obtained with air and sulphurous acid, in which case the product would be sulphuric acid alone.

T. E.

**Laboratory Electrolytic Cells.** By PAUL FUCHS (*Zeit. Elektrochem.*, 1896, **3**, 223).—The author describes three electrolytic cells which are made by Kaehler and Martini. The first consists of an inverted, tubulated bell-jar containing two horizontal discs of platinum gauze which serve as electrodes. The jar is closed air-tight by an ebonite disc, and suitable openings are provided for the escape of gases and for the introduction and removal of the electrolyte. A second form is somewhat similar, except that it is cylindrical, with vertical electrodes which may be separated by a porous pot. The third form consists of several square frames of wood impregnated with oil

and two boards similarly prepared. These may be bolted together so as to form a closed vessel. The object of this construction is to allow of electrodes or diaphragms being fixed across the box in convenient positions by clamping their edges between the frames. T. E.

**Use of Porous Carbon Cylinders in Electrolytic Experiments.** By WALTHER LÖB (*Zeit. Elektrochem.*, 1896, 3, 185).—The results obtained may be summarised as follows. A carbon cylinder, when used in place of a porous earthenware cylinder, acts simultaneously as a porous diaphragm and as an intermediate conductor, one side of it acting as an anode the other as a cathode.

When such a cylinder is used as an electrode, its whole surface is active both within and without, the ions separating in the order of the facility with which they part with their charges whether they are inside or outside the cylinder. If one of the electrodes is placed in metallic contact with the cylinder, the whole system acts as an electrode. T. E.

**Electrolytic Conductivity of Dilute Gases.** By EILHARD WIEDEMANN and GERHARD C. SCHMIDT (*Ann. Phys. Chem.*, 1897, [ii], 61, 737—747).—A discharge was passed through hydrogen chloride gas, and also through the vapours of the haloid salts of mercury, under such conditions that the products appearing at the two electrodes could be collected and examined. The experiments point conclusively to the view that the conductivity of dilute gases is not electrolytic, for in some cases the products of the decomposition do not separate on the electrodes, and in others they appear in amounts quite different from those required by Faraday's law. H. C.

**Specific Electric Conductivities and Freezing Points of Solutions of Water in Formic Acid.** By VLADIMÍR NOVÁK (*Phil. Mag.*, 1897, [v], 44, 9—20).—Owing to the ease with which formic acid absorbs water, and the rapidity with which the resistance of the strong acid changes, it was not found possible to determine the conductivity of the anhydrous acid. With solutions containing from 0·58 to 24 per cent. of water, however, the conductivity was determined at several temperatures, and the value at the freezing point of the solution obtained by extrapolation. It is found, if these values be taken as ordinates and the freezing temperatures as abscissæ, that the points, with the exception of those for the three lowest concentrations, fall upon a straight line of which the equation is $c = 64{\cdot}77 - 6{\cdot}937t$. The specific conductivity of the anhydrous acid cannot be obtained from this equation, but as calculated by extrapolation from the three lowest concentrations, the value $1{\cdot}5 \times 10^9$ at 8·52° (in terms of mercury at 8·52°) is obtained, a result in accord with experiments of Saposchnikoff. The depression of the freezing point is also proportional to the *percentage* of water, and is calculable by the equation $t = 8{\cdot}52 - 1{\cdot}537p$, from which it is clear that the molecular depression is only constant at low concentration. The temperature coefficient of the conductivity was found to be about 0·020 for all the solutions. L. M. J.

**Electrical Conductivity of Salts in Various Solvents.** By Carlo Cattaneo (*Rend. Accad. Linc.*, 1895, ii, 63—70, 73—77).—In continuation of his previous work (Abstr., 1896, ii, 231), the author has determined the electrical conductivity of a number of inorganic salts in methylic, ethylic, and amylic alcohols, acetone, acetic acid, ether, and water solutions, and arrives at the following conclusions. The electrical conductivity of aqueous salt solutions is, in general, greater than those of the corresponding alcoholic solutions, which, in turn, are greater than those of glycerol solutions, and the latter greater than those of ethereal solutions of the same concentration. The electrical conductivities of salt solutions in water, methylic, ethylic, and amylic alcohols, glycerol and acetone do not increase proportionally with the temperature, but rather more slowly; the conductivities of the ethereal solutions, however, with a few rare exceptions, increase more rapidly than the temperature. The molecular conductivity of salts in aqueous solution increases with increased dilution, and the same is true of solutions of the chlorides in alcohol or glycerol and of mercuric iodide in ethylic, methylic, and amylic alcohols, or acetone; the molecular conductivity in ethereal solution decreases, in general, with increased dilution. The temperature coefficient is greater for aqueous than for alcoholic solutions, whilst the coefficients in ethereal solution are of the same order of magnitude as in water, but of negative sign; the coefficients in glycerol solutions are high. The solvent greatly influences the molecular conductivity of a dissolved salt, but no direct relation could be established, and it is shown that the order of conductivity is not the same in the different solvents. Mercuric iodide has a greater molecular conductivity in methylic, than in ethylic, alcohol. The experimental numbers do not confirm Ostwald's dilution law, and no relation could be established between the molecular conductivity and the molecular weight, coefficient of internal friction, or dielectric constant of the various solvents. Further, it seems that the ionic velocities are not wholly independent of the nature of the solvent.

W. J. P.

**New Physical Method of Determining Constitution.** By Paul Drude (*Ber.*, 1897, 30, 940—965).—The extent to which rapidly oscillating electrical vibrations are absorbed during their passage through chemical substances, is highly characteristic of the constitution of the latter, and can be used for determining it. Conductors are electrically absorbent, and the absorption decreases as the electrical vibrations become more rapid; with $4 \times 10^8$ vibrations per second, the electrical absorption of water is negligably small, whilst that of aqueous copper sulphate can be detected in solutions of more than 0·5 per cent. concentration. This so-called "normal" electrical absorption which accompanies conduction is negligable in organic compounds. Electrical vibrations of high frequency are strongly absorbed by the alcohols, amylic alcohol being as strongly absorbent as an aqueous solution of 20,000 times the conductivity; this the author ascribes to "abnormal" electrical absorption, and finds that, whilst the normal absorption decreases as the frequency of vibration increases, the abnormal electrical absorption increases with the speed of vibration. All the

alcohols are strongly absorbent to vibrations of $4 \times 10^8$ per second, but the isomeric ethers are non-absorbent; the conclusion is therefore drawn that, with the exception of water, all liquids containing hydroxyl show abnormal electrical absorption, whilst those containing no hydroxyl are in general non-absorbent. Phenyl ethyl ketone and monobromonaphthalene are slightly absorbent, and the behaviour of these substances and of water are the most notable exceptions to the general rule; the apparently anomalous behaviour of a number of the ketones examined is probably due to tautomerism. Abnormal electrical absorption is shown by concentrated solutions of many hydroxylic compounds, such as sugar; in aqueous solution, acetaldehyde shows considerable electrical absorption.

Although the method now described affords no certain means of identifying hydroxylic compounds, it may, in doubtful cases, prove a valuable guide. The method and apparatus employed will be described at length in a later paper; only about 0·75 c.c. of material is required.

W. J. P.

**Conductivity of Carbon for Heat and Electricity.** By L. Cellier (*Ann. Phys. Chem.*, 1897, [ii], 61, 511—526).—Four specimens of carbon were examined:—I. Graphite of density 1·698. II. Electric light carbon of density 1·467. III. Ditto of density 1·567 IV. Gas retort carbon of density 1·627. The results are given in the following table, in which $T$ is the temperature, $K_w$ the heat conductivity, $K_e$ the electrical conductivity, and $c_1$ the specific heat for unit volume.

| | $T$. | $c_1$. | $K_w$. | $K_e$. | $K_w/K_e$. |
|---|---|---|---|---|---|
| I. | 6·84° | 0·3055 | 0·701 | $13·049 \times 10^{-9}$ | $53·72 \times 10^6$ |
| II. | 9·04 | 0·2488 | 0·367 | $146·32 \times 10^{-9}$ | $2·509 \times 10^6$ |
| III. | 7·83 | 0·2667 | 0·494 | $267·88 \times 10^{-9}$ | $1·844 \times 10^6$ |
| IV. | 9·04 | 0·2782 | 0·400 | $185·36 \times 10^{-9}$ | $2·158 \times 10^6$ |

Weber has shown that for the metals, $K_w/K_e = a + bc_1$, where $a = 5·28 \times 10^4$ and $b = 8·19 \times 10^4$. It is evident that this relationship does not hold in the case of carbon, and that the heat conductivity is 15 or 20 times greater than would be looked for in a metal. H. C.

**Comparison of Rowland's Mercury Thermometers with a Griffiths' Platinum Thermometer.** By C. W. Waidner and F. Mallory (*Phil. Mag.*, 1897, [v], 44, 165—169).—The values for the mechanical equivalent of heat obtained by the mechanical and electrical methods differ by an amount too great to be ascribed to experimental errors. The authors, therefore, compared the mercurial thermometers employed by Rowland with a Griffiths platinum thermometer, the comparison of which with the air scale has been carefully investigated by Callender and Griffiths (Abstr., 1891, 1146). Curves are added giving the corrections to be applied to Rowland's thermometers to reduce the readings to the air scale. These corrections are, however, insufficient to account for the difference in the values of the mechanical equivalent. L. M. J.

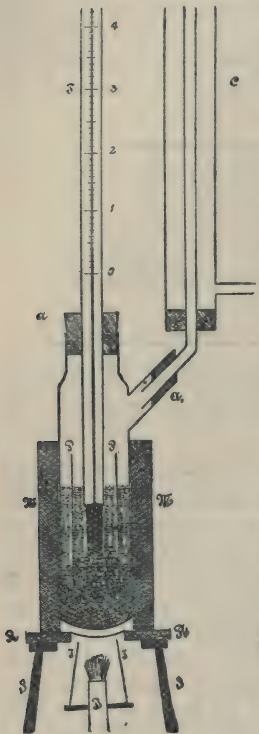
**A Recalculation of Rowland's Value of the Mechanical Equivalent of Heat in Terms of the Paris Hydrogen Thermometer.** By W. S. DAY (*Phil. Mag.*, 1897, [v], 44, 169—172).—The thermometers used by Rowland were compared with three thermometers which had themselves been carefully compared with the hydrogen scale of the International Bureau of Weights and Measures. As, in the comparison, the thermometers were placed horizontally, whereas they were used vertically by Rowland, corrections for compressibility had to be applied. The values for the mechanical equivalent thus obtained are given below.

| Temperature. | Old value. | Corrected value. | Electrical method. |
|---|---|---|---|
| 6° | $0.4209 \times 10^4$ | $0.4204 \times 10^4$ | |
| 15° | $0.4189 \times 10^4$ | $0.4189 \times 10^4$ | $0.4199 \times 10^4$ |
| 25° | $0.4173 \times 10^4$ | $0.4177 \times 10^4$ | $0.4187 \times 10^4$ |
| 35° | $0.4173 \times 10^4$ | $0.4174 \times 10^4$ | |

The corrected values still differ considerably from those obtained electrically; this the author considers to be due to errors in the electrical standards. L. M. J.

**Boiling-point Apparatus for use with Solvents of Low and High Boiling-point.** By HARRY CLARY JONES (*Amer. Chem. J.*, 1897, 19, 581—597).—The apparatus consists of a boiling-vessel, A, of much the usual form, 18 cm. long by 4 cm. in diameter, closed at the bottom, and cylindrical in shape, but narrowing to about $2\frac{3}{4}$ cm. at the neck, which is ground to receive a glass stopper; just below the shoulder there is a side tube, *a*, 2—$2\frac{1}{4}$ cm. in diameter; to this the condenser, *c*, which is about 40 cm. long, is attached by means of a cork. Up to this side tube, the vessel is surrounded by a close-fitting mantle, m, 12 cm. high by $1\frac{1}{2}$ cm. thick; this consists of an inner layer of thin asbestos-cardboard secured with copper wire, round which thick asbestos paper is wrapped until the desired thickness is attained. The apparatus stands on an asbestos ring, R, supported on a tripod, S; this ring is about 9 cm. in external diameter, and has in the centre a circular hole, about $3\frac{1}{2}$ cm. in diameter, over which a piece of fine copper gauze is placed; the glass bottom of the boiling vessel rests on this gauze, and is heated by a Bunsen burner underneath. The bottom of the vessel is filled with glass beads; down into these, to the depth of $\frac{1}{2}$—1 cm., is pushed a platinum cylinder, P, 8 cm. high by $2\frac{1}{2}$ cm. wide; this can be made simply by rolling up a piece of platinum foil and fastening it, but it is better that the edges should be welded. Inside the cylinder, and on the top of the glass beads, are placed some pieces of platinum foil about $\frac{3}{4}$ cm. square and with the corners bent alternately up and down. In the actual experiment, the bulb of the thermometer is situated within the cylinder, and so has platinum all round it, and below; this prevents radiation. Further, the apparatus is never filled to such a level that the liquid in it can boil over the top of the platinum cylinder; the cooled solvent flowing back from the condenser

cannot thus come into direct contact with the thermometer, but has first to pass down and up through the beads, by which process it is heated to the proper boiling point of the solution. These are the two distinctive points of the apparatus, and to them is attributed the fact that it gives more concordant results than other forms.



In making an experiment, the stopper is placed in the neck of the vessel, the side tube is closed with a cork, and the whole is weighed. A suitable quantity of solvent is then introduced, and the whole reweighed. The stoppers are then removed, the condenser is inserted into the side tube, and the Beckmann thermometer, by means of a cork, into the neck of the vessel, and the boiling point of the solvent is determined in the usual way. Some of the substance to be experimented with, in the form of pellets, is shaken from a tared tube into the apparatus, either through the condenser, or through the neck if the solvent is but little volatile; and the boiling point is again determined. Great care must be taken that the liquid boils quietly but very actively; boiling of an explosive character must be avoided. A small hand lens should be used in reading the thermometer and the latter should be tapped once or twice with a pencil just before the temperature is read. The time that elapses before the thermometer becomes stationary is much greater in the case of the pure solvent than in that of the solution.

In the results quoted below, each pair of numbers represents a series of determinations of the molecular weight, the numbers quoted being the lowest and highest values obtained. The names of the solvents are printed in italics, those of the dissolved substances in ordinary type; the true molecular weights are printed in brackets.—*Ether;* naphthalene (128): 126·9—128·8, 126·5—126·9. *Alcohol*; $NHPh\cdot P(NPh)_2$ (305): 298—306. *Benzene*; naphthalene: 133·0—135·4, 133·7—137·4, 133·0—134·0, 135·1—136·4. *Anisoil*; acetanilide (135): 173·0—176·7, 170·4—179·4; *anthracene* (178): 201·0—205·1 198·7—207·9. *Aniline*; triphenylmethane (244): 238·6—247·4, 237·0—242·6; diphenylamine (169): 167·1—174·1. C. F. B.

**Thermochemistry of Copper Compounds.** By PAUL SABATIER (*Compt. rend.*, 1897, **125**, 301—305).—Anhydrous cupric oxide readily soluble in acids is obtained by heating at 440°, for 7 or 8 hours, the brown hydroxide obtained by precipitation at 100°. The difference between the heat of dissolution in acids of this oxide and that obtained by strongly heating is +2·0 Cal.

The heat of neutralisation of the oxide, corrected for the thermal disturbance resulting from the action of dilute acids on solutions of cupric salts are,

| | Dried Oxide | Hydroxide Brown | Hydroxide Blue |
|---|---|---|---|
| Nitric acid........... | 16·2 Cal. | 16·4 Cal. | 15·9 Cal. |
| Hydrochloric acid ... | 16·4 " | 16·6 " | 16·1 " |
| Hydrobromic acid ... | 16·1 " | 16·3 " | 15·8 " |
| Sulphuric acid ...... | 19·2 " | 19·4 " | 18·9 " |

These results show that CuO dried + $\frac{1}{4}H_2O$, solid = $\frac{1}{4}Cu_4H_2O_5$ develops − 0·5 Cal., and CuO, dried + $H_2O$, solid = $Cu(OH)_2$ develops − 1·1 Cal.

The heat of dissolution of the nitrate, $Cu2NO_3 + 6H_2O$, was found to be − 10·5 Cal. at about 15°, and since that of the hydrate $Cu2NO_3 + 3H_2O$ is − 2·5 Cal. (Thomsen) it follows that $Cu(NO_3)_2,3H_2O + 3H_2O$ solid = $Cu(NO_3)_2,6H_2O$ develops + 3·9 Cal. (1·3 × 3)

The hexahydrate loses half its water by efflorescence, and this agrees with the author's previous observation that many chlorides lose by efflorescence any water of hydration the heat of combination with which is lower than 2·0 Cal.

The following numbers were obtained for the heat of dissolution of the basic salts in the corresponding dilute acids; basic nitrate + 34·0 Cal., basic sulphate + 48·0 Cal., basic bromide + 32·4 Cal., and the following results can be deduced.

$Cu(NO_3)_2 + 3CuO$ dried = $Cu(NO_3)_2,3CuO$ develops + 14·6 Cal.
$Cu(NO_3)_2,3H_2O$, solid + 3CuO dried = $Cu(NO_3)_2, 3Cu(OH)_2$ develops + 12·1 Cal.
$CuSO_4$ diss. + $3Cu(OH)_2 = CuSO_4,3CuO,4H_2O$, develops + 5·9 Cal.
$CuSO_4,H_2O$ cryst. + $3Cu(OH)_2 = CuSO_4,3CuO,4H_2O$, develops + 15·2 Cal.
$CuBr_2$ diss. + $3Cu(OH)_2 = CuBr_2,3Cu(OH)_2$, develops + 14·2 Cal.
$CuBr_2$, solid + $3Cu(OH)_2 = CuBr_2,3Cu(OH)_2$, develops + 22·2 Cal.

The heat of dissolution of anhydrous cupric bromide is + 7·9 Cal. at 12° and + 8·8 Cal. at 24°.

It will be observed that, except in the case of the sulphate, the heat of formation of the basic salts is considerable. The smaller development of heat in the case of the sulphate agrees with the known fact that basic sulphates containing lower proportions of oxide can be prepared.

C. H. B.

**Thermochemistry of Mercury Salts.** By RAOUL VARET (*Ann. Chim. Phys.*, 1896, [vii], 8, 79—141).—In the first chapter of this memoir, dealing with compounds of mercury with the elements, the heats of formation of mercurous and mercuric chlorides, bromides, iodides, and oxides are given (Abstr., 1895, ii, 305, 380, 381). The following heat of formation of mercuric sulphide is recorded :—Hg liq. + S sol. = HgS ppt. develops + 10·6 Cal. Numbers representing the thermal disturbances accompanying the isomeric change of mercuric sulphide are also given (Abstr., 1895, ii, 435). The second chapter deals with the thermochemistry of mercuric sulphate, basic mercuric sulphate (Abstr., 1895, ii, 103), and mercurous sulphate (Abstr., 1895, ii, 380). For mercurous sulphate, the following additional numbers are given.

$Hg_2O$ sol. + $SO_3$ sol. = $Hg_2SO_4$ sol. develops + 49 Cal.
$Hg_2O$ sol. + $H_2SO_4$ diss. = $Hg_2SO_4$ sol. + $H_2O$ liq. develops + 11·8 Cal.
$Hg_2O$ sol. + $H_2SO_4$ liq. anhyd. = $Hg_2SO_4$ sol. + $H_2O$ liq. dev. + 28·8 Cal.

The third chapter deals with the nitrates of mercury, the heats of formation and of dissolution of mercuric nitrate and basic mercuric nitrate being given (Abstr., 1895, ii, 154), as also those of mercurous nitrate (Abstr., 1895, ii, 380). For the latter salt, the following additional numbers are recorded.

$Hg_2O$ sol. + $3HNO_3$ diss. = $Hg_2(NO_3)_2$ diss. + $HNO_3$ diss- + $H_2O$ liq. dev. + 6·23 Cal.
$Hg_2O$ sol. + $2HNO_3$ diss. = $Hg_2(NO_3)_2,2H_2O$ sol. develops + 18·63 Cal.

The fourth chapter contains an account of the preparation, properties, and thermochemistry of mercuric picrate (Abstr., 1895, i, 131) and of mercurous acetate (Abstr., 1895, ii, 381). The following additional observations are recorded.

$Hg_2O$ sol. + $2C_2H_4O_2$ diss. = $Hg_2(C_2H_3O_2)_2$ sol. + $H_2O$ liq. dev. + 14·73 Cal.
$Hg_2O$ sol. + $2C_2H_4O_2$ sol. = $Hg_2(C_2H_3O_2)_2$ sol. + $H_2O$ liq. „ + 11·93 Cal.
Hg liq. + $Hg(C_2H_3O_2)_2$ sol. = $Hg_2(C_2H_3O_2)_2$ sol. „ + 5·20 Cal.

A. C. C.

**Isothermals of Isopentane.** By J. Rose-Innes (*Phil. Mag.*, 1897, [v], **44**, 76—82).—The experiments of Young (*Proc. Phys. Soc.*, 1894, 602) give a complete series of isothermals for isopentane, and the author endeavoured to find a suitable equation to represent these curves. Making use of Ramsay and Young's relation that $p = bT - a$ at constant volume, it is evident that $pv = RT$ only at temperature $T = a(b - R/v)$. This temperature is, however, seen from Young's results to be practically constant for a very large range of volumes, namely, from 8 to 350. Confining the investigation to volumes above 3·4, the author finds the values $a = l \div v(v+k)$ and $b = R/v \times \{1 + e \div (v + k - g/v^2)\}$ give satisfactory results where $l$, $k$, $e$, and $g$ are constants whose values are given. From the equation thus obtained, by determining the value of $v$ where $dp/dv$ and $d^2p/dv^2$ vanish, the critical volume is obtained, and hence the critical temperature and pressure. The numbers calculated in this way are critical vol. = 4·5, critical temp. = 191·7°, critical pressure = 26250; these agree satisfactorily with the experimental results obtained by Young.

L. M. J.

**Melting Points of Organic Substances.** By Antoine P. N. Franchimont (*Rec. Trav. Chim.*, 1897, **16**, 126—161).—From a careful and detailed study of the relations existing between the composition of substances and their melting points, the author deduces certain rules, to which, however, there are many exceptions, but doubtless a number of these will disappear on closer investigation.

In general, the melting point of an organic compound *increases* (*a*) when two atoms of hydrogen connected to the same carbon atom are replaced by an atom of oxygen; (*b*) when an atom of hydrogen is replaced by the groups OH or $NH_2$; (*c*) when 3 atoms of hydrogen connected to the same carbon atom are replaced by a nitrogen atom; and *decreases* when an atom of hydrogen connected to an oxygen or

carbon atom, or a hydrogen atom of an $NH_2$ group, is replaced by the group $CH_3$. In the case of hydrogen, connected to a carbon atom, or in an $NH_2$ group, this is only strictly true of the first atom replaced; for although carbamide melts at 132° and methylcarbamide at 102°, the dimethyl derivative melts at 180°.

By introducing a $CH_3$ group into a compound, the symmetry of the latter is more or less altered, and this fact has a great influence on the melting point. For example, in malonic acid, the symmetry is modified by the introduction of one $CH_3$ group, and is re-established by a second, as is seen from the following.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| H | | COOH | $CH_3$ | | COOH | $CH_3$ | | COOH |
| | C | | | C | | | C | |
| H | | COOH (134°) | H | | COOH (130°) | $CH_3$ | | COOH (180°). |

The effect on the melting point is a lowering in the first place but an increase in the second, and this effect is more marked when an ethyl or higher alkyl group is substituted for hydrogen; ethylmalonic acid melts at 111·5° and the diethyl derivative at 125°. It is evident, therefore, that by the partial re-establishment of the symmetry of a compound, its melting point is increased.

In 1872, the author, in conjunction with Zincke, pointed out that nonylic acid melts at a lower temperature than octoic acid, so that in a homologous series the melting point is not always augmented with increase in carbon; and the possibility was suggested that acids containing an even number of carbon atoms have a relatively higher melting point than those with an uneven number. A similar fact is noticeable in the case of the normal aliphatic hydrocarbons, where in passing from a hydrocarbon with an even number of carbon atoms to the next higher homologue with an uneven number, the melting point does increase, but to a much less degree than in passing from a hydrocarbon with an uneven number of carbon atoms to the next higher member with an even number. It is not certain if this phenomenon is general among normal aliphatic compounds, although it would appear probable, as it is not limited to the above examples. Symmetry here again plays an important part, for in compounds with an even number of carbon atoms (and higher melting point), the symmetry is more perfect than in those with an uneven number of carbon atoms, if a molecule is considered as consisting of two equal parts which have a symmetry with regard to a plane dividing the molecule in half.

Concerning the effect produced on the melting point of a substance when a $CH_2$ group replaces two hydrogen atoms attached to the same carbon atom or CH replaces three hydrogens, facts which throw any light on the subject are almost totally wanting. In unsaturated hydrocarbons derived from saturated ones by replacement of two hydrogens of a $CH_3$ group by $CH_2$, it is noticed that the melting point decreases, and where the unsaturated is derived from the saturated hydrocarbon by the replacement of three hydrogens of a $CH_3$ group by CH, the melting point increases.

The substitution of one hydrogen atom by chlorine, bromine, or iodine lowers the melting point, those cases in which an elevation has been observed being exceptional, and, probably, symmetry again plays

an important part. More than one halogen atom increases the melting point, and if the entering atoms are attached to different carbon atoms the relative distance has an effect.

The entrance of such groups as NO, NOH, or $NO_2$ into a compound usually produces an increase in the melting point. A. W. C.

**Condensation and Critical Phenomena of some Substances and Mixtures.** By J. P. Kuenen (*Phil. Mag.*, 1897, [v], 44, 174—199).—A continuation of the author's previous paper on the critical phenomena of ethane and nitrous oxide (Abstr., 1896, ii, 10). The critical values obtained for the ethane (32·05° and 48·8 atms.) differ from those previously obtained by other observers, and the author therefore investigated the purity of ethane produced by various methods. He considers it impossible to obtain pure ethane by the reduction of ethylic iodide, and finds that the purest gas is obtained by the electrolysis of sodium acetate, using Murray's method (Trans., 1892, 10).

According to Dewar (Abstr., 1880, 843), the critical temperature of a mixture of equal parts of carbonic anhydride and acetylene is higher than that of either of the constituents, but this result is found to be incorrect, and was due to an impurity in the acetylene. The author finds the critical temperature and pressure of carefully purified acetylene to be 35·25° and 61·02 atmospheres respectively, and for the mixture the critical temperature lies between those of the constituents. In the case of mixtures of ethane and acetylene, the critical temperature attains a minimum value for the mixture containing 0·53 ethane with 0·47 acetylene, which is also very nearly the mixture possessing a maximum vapour pressure. Retrograde condensation of the first kind was also well observed in these mixtures. In the case of ethane and carbonic anhydride, the minimum critical temperature occurs for 0·45 ethane, and maximum vapour pressure for 0·30 ethane. The author applies van der Waals' equation to the case of mixtures, and, regarding the constant $a_x$ to be given by the expression $a_x = a_1(1-x)^2 + 2a_{12}x(1-x) + a_2x^2$, with a similar expression for $b_x$, deduces the values $a_{12}$ and $b_{12}$ from the critical values of one mixture, and from these, the critical values of other mixtures, supposed to remain undivided, are calculated. L. M. J.

**A New Form of Pyknometer.** By J. C. Boot (*J. Amer. Chem. Soc.*, 1897, 19, 61—62).—A great inconvenience in using the ordinary form of specific gravity bottle is that, on drying the outside or during the weighing, a portion of the liquid is liable to run out, particularly if the temperature of the room is higher than that of the liquid. The author now uses a double-walled pyknometer, in which the space between the two walls is carefully exhausted. This apparatus can be carefully dried and weighed without any liquid escaping through the capillary tube. L. de K.

**Contraction of some Organic Compounds on Solidification.** By Adolf Heydweiller (*Ann. Phys. Chem.*, 1897, [ii], 61, 527—540).—The contraction taking place on the solidification of benzene, phenol, menthol, thymol, stearic acid, and naphthalene was directly measured

in a dilatometer. The differences in the specific volumes of the liquid and solid $v_f - v_s = \Delta v$ were as follows:—For benzene at 5·35°, between 0·1219 and 0·1304; for phenol at 40·80°, between 0·0461 and 0·0540; for menthol at 41·37°, between 0·0485 and 0·0653; for thymol at 49·41°, between 0·0572 and 0·0709; for stearic acid 0·1387 at 67·78°; and for naphthalene at 79·86°, between 0·1241 and 0·1454. H. C.

**Volume of Vapour produced from One Cubic Centimetre of a Liquid at the Boiling Point.** By J. A. GROSHANS (*Ann. Phys. Chem.*, 1897, [ii], **61**, 780—789).—The volume of vapour produced from 1 c.c. of a liquid at the boiling point $T$ in absolute temperature is given by $81·78 \times T/MV$, where $MV$ is the molecular volume of the liquid. For compounds of similar composition, this quantity is practically constant, but varies in the case of compounds belonging to the same homologous series. These variations are, however, accounted for by the author on the basis of his previously published work on homologous compounds. H. C.

**Reciprocal Diffusion of Electrolytes in Dilute Aqueous Solutions.** By U. BEHN (*Ann. Phys. Chem.*, 1897, [ii], **62**, 54—67).—The author determines the relative amounts of the ions which diffuse across the boundary between two dilute solutions of one or more binary electrolytes. As cases of electrolytes in solutions of equal concentration, the two combinations of HCl—LiCl and $HNO_3$—$AgNO_3$ were selected. These were taken in decinormal solutions. Diffusion under the influence of a fall in concentration was studied more especially with solutions of silver nitrate containing free nitric acid. The theories of hydro-diffusion developed by Nernst and Planck were applied to the results, but no satisfactory agreement obtained, a fact which the author ascribes to the impossibility of sufficiently preventing the formation of currents in the solutions. H. C.

**Diffusion Coefficients of Sodium Chloride Solutions of various Concentrations.** By L. MARINI (*Rend. Accad. Linc.*, 1895, ii, 135—139).—Using a spectrometric method somewhat similar to that proposed by Wiener (*Ann. Phys. Chem.*, 1893, [ii], vol. 49), the author has determined the diffusion coefficient of sodium chloride in 2N, N, N/2, and N/5 aqueous solutions as 1·109, 1·078, 1·065, and 1·069 at 18° respectively. W. J. P.

**The Ionising Power of Solvents.** By W. C. DAMPIER WHETHAM (*Phil. Mag.*, 1897, [v], **44**, 1—9).—The ionising power of a solvent was shown by Nernst to be intimately connected with its dielectric constant (Abstr., 1894, ii, 266). Of all liquids hitherto examined, water possesses the highest dielectric constant and the greatest ionising power, but the author hoped that, by examining solutions of water in other liquids, indication of its dissociation might be obtained. Determinations were made of the resistances of various solutions of water in formic, acetic, and trichloracetic acids, and it is noticeable that, of these solvents, formic acid alone possesses a dielectric constant approaching that of water ($K = 62$; $K_{H_2O} = 75·5°$, Thwing). Curves of conductivity against percentage of water are given, which show that, in the acetic and trichloracetic acid solutions, the forms of the

ascending and descending portions are totally different; the former, that is the curve for the solution of water in acid, cutting the conductivity axis at right angles and ascending rapidly when the concentration reaches 10 to 20 per cent. With formic acid, on the other hand, the ascending portion is a straight line to 60 per cent. of water, and although it does not resemble the descending part, it shows that even dilute solutions of water in formic acid have considerable conductivity. The author considers that these solutions are essentially different from normal electrolytic solutions, and hence that the water is not dissociated, a view confirmed by cryoscopic observations. The conductivity of the formic acid solutions, however, renders it probable, in the author's opinion, that, in a solvent of higher dielectric constant, the water itself would be dissociated. L. M. J.

**Affinity Constants and Heat of Dissociation of some Nitrogen Acids.** By E. Baur (*Zeit. physikal. Chem.*, 1897, **23**, 409—416).—Jahn found that the affinity constant of the first five fatty acids increases by about 5 per cent. between 10° and 40°, whilst Euler's results show that that of the aromatic carboxy-acids increases by about 10 per cent. between 0° and 50°. As, however, some nitrogen compounds appear to have a greater variability, the author determined the constant for nitrocarbamide, $NH_2\cdot CO\cdot NH\cdot NO_2$, nitrourethane, $EtO\cdot CO\cdot NH\cdot NO_2$, amidotetrazole, $CN_4H\cdot NH_2$, benzenesulphonitramine, $C_6H_5\cdot SO_2\cdot NH\cdot NO_2$, and their sodium salts. The conductivity was measured at 0°, 10°, 20°, 30°, 40° and 50° at various dilutions, and the affinity constant for each temperature calculated by Ostwald's formula. The benzene sulphonitramine, however, was so strongly dissociated at 0°, that no further determinations were taken. In each case investigated, the temperature coefficient was very great, the constant increasing to the extent of 85 per cent. for 20° in the case of nitrocarbamide and by 100 per cent. and 200 per cent. respectively for 40° in the cases of nitrourethane and amidotetrazole. If this high temperature coefficient should prove to be characteristic of compounds in which the acidic hydrogen is united to nitrogen, it might prove of service in the determination of constitution. The heat of dissociation of the compounds was also determined by Nernst's equation with the following results.

| | Nitrocarbamide. | Nitrourethane. | Amidotetrazole. |
|---|---|---|---|
| 5° | 5477 cal. | 3665 cal. | 4724 cal. |
| 25° | 3640 ,, | 2943 ,, | 4593 ,, |

L. M. J.

**Relation between the Polymerisation of Liquids and their Power of Dissociating Electrolytes.** By Paul Dutoit and Emily A. Aston (*Compt. rend.*, 1897, **125**, 240—243).—All the solvents which yield solutions having a high electrical conductivity contain the hydroxyl group, but these are also the compounds which, according to the results obtained by Ramsay and Shields, and other evidence, are

polymerised in the liquid state. The authors have determined the electrical conductivity of solutions of several metallic salts and organic acids in propionitrile, acetone, methyl ethyl ketone, methyl propyl ketone, and nitroethane, which are not hydroxyl derivatives, but yet are shown by evidence of various kinds to be polymerised in the liquid state. In all cases, the conductivites are high, and these results, when compared with the low conductivities observed by Kablukoff in solutions of electrolytes in non-polymerised solvents, seem to show clearly that there is a general relation between the dissociating power of a solvent and its polymerised or non-polymerised condition, as the case may be. C. H. B.

**Decomposition of Silver Salts by Pressure.** By J. E. Myers and Ferdinand Braun (*Phil. Mag.*, 1897, [v], **44**, 172—173).—It has been shown by Carey Lea that silver salts may be decomposed by pressure (Abstr., 1894, ii, 85), and the authors determined the electromotive force developed when this decomposition is effected between silver and platinum electrodes. The pressure employed was about 3000—5000 atmospheres, and the E.M.F. was found to attain a maximum value varying with the salt, and being approximately: silver bromide, 0·07; silver chloride, 0·03; and silver iodide, 0·04; the values being given in terms of the E.M.F. of a Daniell's cell. Silver nitrate and potassium bromide were not affected singly, but together gave an E.M.F. of about 0·08. The resistance also increased considerably during the compression. L. M. J.

**Decomposition of Triglycerides by Bases and Dilute Acids.** By Adolf C. Geitel (*J. pr. Chem.*, 1897, [ii], **55**, 429—456).—By the application of the law of mass action to the decomposition of triglycerides by bases and acids, the author arrives at the conclusion that the decomposition, and therefore the formation, of these compounds takes place in stages, the reactions being all bimolecular in the sense of the equations,

$$C_3H_5(OH)_3 + HAc = C_3H_5(OH)_2Ac + H_2O,$$
$$C_3H_5(OH)_2Ac + HAc = C_3H_5(OH)Ac_2 + H_2O,$$
$$C_3H_5(OH)Ac_2 + HAc = C_3H_5Ac_3 + H_2O.$$

In order to apply the law of mass action to each of the separate reactions in the mixture, a full mathematical consideration of the case is entered on, this necessarily taking a somewhat complex form. H. C.

**Inversion of Sugar by Salts.** By John H. Long (*J. Amer. Chem. Soc.*, 1896, **18**, 693—717).—This is a continuation of the work previously described (Abstr., 1896, ii, 414). A 20 per cent. solution of sugar was mixed with varying quantities of each salt and heated at 85°, the progress of the inversion being polarimetrically determined at intervals. The results show that, with most of the salts, the inversion coefficient varies with the time. In the case of alum, it is constant throughout; with ferrous sulphate, ferrous ammonium sulphate, zinc sulphate, and cadmium chloride, it increases slowly; with manganous sulphate, manganous chloride, and lead nitrate it increases

rapidly; whilst with ferrous chloride, ferrous bromide, and ferrous iodide, it decreases rapidly. This irregular behaviour probably bears some relation to the stability of the salts in aqueous or weak saccharine solutions. The solutions of the last three salts become turbid at first but clear afterwards, whilst in the solutions of ferrous sulphate and ferrous ammonium sulphate the turbidity is persistent. Manganous sulphate is also slightly decomposed and the decomposition increases with time and temperature. The solutions with manganous chloride, cadmium chloride, and lead nitrate remain clear, but the first soon loses its pink colour and this is not restored on cooling. Here obviously some change in the form of combination of the manganese has taken place and probably in most cases formation of compounds of the base with the sugar interferes with the regularity of the rate of inversion. E. W. W.

**Washing Bottle for Gases.** By SEBASTIANO FAMULARI (*Gazzetta*, 1897, **27**, ii, 58—59).—This is a description of a simple washing bottle for gases in which the author states that the gas is caused to pass twice through the same washing liquor.

W. J. P.

## Inorganic Chemistry.

**The Commencement of the Combination of Hydrogen with Oxygen.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1897, **125**, 271—275).—The author has made experiments with a view of ascertaining the exact nature of the influence exerted on the combination of oxygen and hydrogen by the walls of the vessel in which the gaseous mixture is contained. In all cases, the hydrogen and oxygen were mixed in the proportion of 2 volumes of the former and 1 volume of the latter. In contact with dry barium oxide, there is no combination at the ordinary temperature, nor at 100° or 182°; but at 250°, 77 per cent. of the gaseous mixture disappeared in 5 hours, and at 280°, the whole of the gas disappeared after 26 hours. Further experiments showed, however, that at first the oxygen disappears more rapidly than the hydrogen, part of it combining with the barium oxide to form the peroxide, which is subsequently reduced by the hydrogen. At 280°, for example, all the oxygen disappeared after 5 hours, but 16 per cent. of the hydrogen remained; the latter was, however, gradually absorbed. The influence of the barium oxide is of the same order as that exerted by platinum.

Potassium hydroxide behaves similarly, combination taking place slowly at 250°, and somewhat rapidly at 280—300°. The glass is somewhat strongly attacked and alkali manganates derived from the manganese in the glass are formed. In this case, also, the oxygen at first disappears more rapidly than the hydrogen, owing to the formation of peroxides and manganates.

Direct experiments show that in presence of a very small quantity of water, glass absorbs relatively considerable quantities of oxygen, but no such absorption takes place with a larger proportion of water.

The intermediate formation of alkali peroxides no doubt plays an important part in the combination of hydrogen and oxygen when heated in glass vessels. C. H. B.

**Electrolytic Formation of Persulphuric Acid.** By FRANZ RICHARZ (*Ber.*, 1897, **30**, 1826—1827).—*Apropos* of Nernst's lecture (this vol., ii, 394), the author recalls the fact that already in 1884—1888, he had investigated and explained the above reaction. He has also shown (Abstr., 1896, ii, 585) that, with dilute sulphuric acid, the attainment of a potential difference of 1·08 volts. is characterised, not only by a sudden rise in the strength of the current (as was observed long ago by Helmholtz), but also by the setting-in at the cathode of the formation of hydrogen peroxide by reduction of dissolved neutral oxygen. C. F. B.

**Atomic Weights of Nitrogen, Chlorine, and Silver.** By ANATOLE LEDUC (*Compt. rend.*, 1897, **125**, 299—301).—Taking $O = 16$ and $C = 12·004$, the author's determinations of the sp. gr. of gases, combined with the fact that the molecular volume of nitrogen is higher than that of carbonic oxide (*Compt. rend.*, **125**, 297), lead to the conclusion that $N = 14·005$. Stas found $N = 14·044$, but if his results are corrected for the oxygen probably present in the silver used, the number becomes $N = 14·002$. Adopting the author's value for N, the ratio $Ag : NO_3$ is 1·7404, whereas the later experiments of Stas give 1·7400.

The numbers finally adopted by the author are, $O = 16·00$, $N = 14·005$, $H = 1·0076$, $Cl = 35·47$, and $Ag = 107·916$. C. H. B.

**The Different Varieties of Carbon (Amorphous, Graphite, Diamond).** By HENRI MOISSAN (*Ann. Chim. Phys.*, 1896, [vii], **8**, 289—305, 306—347 and 466—558).—A full account is given of the methods of production, modes of occurrence, and general properties of various forms of carbon, the first of the three papers dealing solely with the element in the amorphous state. Carbon prepared by the following methods was studied, (1) by the incomplete combustion of petroleum; (2) by the incomplete combustion of acetylene; (3) by the decomposition of acetylene by detonation with mercuric fulminate; (4) by the action of sulphuric acid on starch; (5) by the action of ferric chloride on anthracene at 180°; (6) by the decomposition of carbon tetriodide at 200°; (7) by the action of light on carbon tetriodide; (8) by the action of a Smithson couple on a solution of carbon protoiodide in carbon bisulphide; (9) by the action of zinc filings on carbon tetriodide; (10) by the action of magnesium on a solution of the tetriodide in carbon bisulphide, and (11) by the action of boron at a red heat on carbonic anhydride. The carbon prepared by all these methods was amorphous and always more or less impure, its complete purification being, if not impossible, at least extremely difficult, owing to the great tenacity with which it retains water, traces of hydrocarbons, and small quantities of the elements present during its separation, such as iodine, lead, zinc, &c. Methods (4) and (5) yielded mixtures of organic compounds rich in carbon, from which it was impossible to obtain the element even moderately pure in the amorphous state. The density of amorphous carbon, by

whatever method prepared, is always less than 2, being 1·76 in the case of the purest, non-ignited lampblack. When heated, amorphous carbon undergoes polymerisation, its ignition point in oxygen being raised and its resistance to the action of chromic acid mixture increased.

The second paper deals with graphite, the first chapter containing an account of samples obtained from Ceylon, Borrowdale, Ticonderoga, Greenville, Omeansk, Mugrau, Scharzbach and Karsok (Abstr., 1896, ii, 165), from an American pegmatite (Abstr., 1896, ii, 182), and from Blue Earth from the Cape (Abstr., 1893, ii, 285). The nature of the carbon existing in meteoric irons is also discussed (Abstr., 1893, ii, 288, 475; 1896, ii, 194). In the second chapter, the rates of oxidation, the ignition points, and the densities of artificially prepared samples of graphite are given (Abstr., 1895, ii, 219), and the displacement of carbon in fused cast-iron by boron and silicon is described (Abstr., 1895, ii, 220). The properties of graphite separated from iron are also given (Abstr., 1895, ii, 220). The third chapter deals with the preparation and properties of intumescent graphite (Abstr., 1893, ii, 320; 1895, ii, 221).

In the first chapter of the third paper, the author gives the properties of the diamond and the composition of the ash left on ignition (Abstr., 1893, ii, 319); the occurrence of diamonds in the Blue Earth from the Cape, in sand from Brazil, and in the meteorite of Cañon Diablo is also discussed (Abstr., 1893, ii, 285; 1897, ii, 46; 1893, ii, 288, and 1896, ii, 194). The second chapter deals with the solubility of carbon in various metals at ordinary pressures and the formation of definite carbides (Abstr., 1893, ii, 275; 1894, ii, 452; 1895, ii, 272, 501; 1896, ii, 364, 419, 422, 423, 428, 606, 608, 609, and 650). The third chapter contains an account of the effect of high temperatures on the different forms of carbon (Abstr., 1894, ii, 42), and of the properties of its vapour (Abstr., 1895, ii, 164). In the fourth chapter, numerous experiments on the artificial production of diamonds are detailed (Abstr., 1893, ii, 275; 1894, ii, 189; 1895, ii, 644), whilst the fifth is devoted to a description of the method adopted for the combustion of artificially prepared diamonds. A. C. C.

**Electrolytic Preparation of a New Class of Oxidising Substances.** By EMIL J. CONSTAM and ARTHUR VON HANSEN (*Zeit. für Elektrochem*, 1896, 3, 137).—It is to be expected that the alkali carbonates will, in very concentrated solutions, dissociate into the ions $\overset{+}{M}$ and $\overset{-}{M}CO_3$, and that the latter will unite to form percarbonates, $M_2C_2O_6$, when liberated by electrolysis at the anode. When a saturated solution of potassium carbonate is electrolysed, the evolution of oxygen diminishes as the temperature falls, ceasing almost completely at $-10°$. At the same time, the precipitate of potassium hydrogen carbonate, which at first forms at the anode, is replaced by a bluish, amorphous powder consisting of potassium percarbonate. In order to obtain a good result, the solution must be saturated and the temperature not allowed to rise above $-10°$ to $-15°$. The current density has no very marked influence on the result. The dried product is a bluish-white, amorphous, deliquescent powder, which is decomposed, when gently heated, into potassium carbonate, carbonic anhydride, and oxygen. It dissolves almost without decomposition in ice-cold water,

but is decomposed by water at the ordinary temperature. It is somewhat soluble in alcohol. It liberates iodine from a solution of potassium iodide, especially after acidification, oxidises lead sulphide to sulphate, bleaches indigo, wool, cotton, or silk, and reduces the peroxides of manganese and lead, and silver oxide, forming the corresponding carbonates and liberating oxygen. With caustic potash, or with dilute sulphuric acid, it yields hydrogen peroxide. The substance, dried over phosphoric anhydride, contains from 53·59 to 77·91 per cent. of potassium percarbonate, the remainder being potassium carbonate, bicarbonate, and water. Rubidium percarbonate was obtained in a similar way. The sodium and ammonium salts could not be obtained in the solid state owing to the comparatively small solubilities of the carbonates. T. E.

**Double Halogen Salts of Cæsium and Rubidium.** By HORACE L. WELLS and H. W. FOOTE (*Amer. J. Sci.*, 1897, **3**, 461—465).—The authors have prepared the rubidium antimony chloride described by Remsen and Saunders (*Amer. Chem. J.*, **14**, 155) to which they gave the formula $23RbCl,10SbCl_3$; the salt is not altered by recrystallisation under varying conditions from strong or dilute hydrochloric acid, or from a solution of hydrogen chloride in alcohol; from this the authors conclude that the substance is not a mixture of two simpler salts. The results obtained on analysis agree more closely with the formula $7RbCl,3SbCl_3$, but the differences between the two formulæ in percentage composition are so slight that it is impossible to decide between them by means of chemical analysis.

*Rubidium antimony oxychloride*, $2RbCl,SbCl_3,SbOCl$, is obtained when the preceding salt is crystallised from very dilute hydrochloric acid; it crystallises in short, colourless prisms.

The double chlorides of bismuth and cæsium described by Remsen and Brigham are formed under the following conditions. The salt $3CsCl,BiCl_3$, separates in colourless plates when cæsium chloride (50 grams), in hydrochloric acid solution, is mixed with bismuth chloride (1 to 25 grams). The salt, $3CsCl,2BiCl_3$, obtained when bismuth chloride (50 grams) is mixed with cæsium chloride (1 to 80 grams), crystallises in pale, yellow needles.

*Cæsium bismuth iodide*, $3CsI,2BiI_3$, is the only double iodide the authors were able to prepare; it is obtained under all conditions when the two iodides are mixed, and is a bright red to reddish-brown, crystalline precipitate which is only very sparingly soluble, especially in an excess of cæsium iodide. E. C. R.

**Silver Peroxynitrate.** By EDUARD MULDER (*Rec. Trav. Chim.*, 1897, **16**, 57—112).—Continuing his researches on the black, crystalline compound of the formula $Ag_7NO_{11}$ (Abstr., 1896, ii, 561), the author has submitted it to the action of heat, and finds that it decomposes at a relatively low temperature, giving off oxygen. In the first series of experiments, extending over 90 days, the substance was heated in a slow current of dry air at a temperature of 52° to commence with, this temperature being gradually increased to 185°. A total loss in weight corresponding with 5 atoms of oxygen was observed, but the elimination of oxygen does not proceed regularly, apparently taking place in at least two phases. Three atoms of oxygen are lost at 51—60°, but

whereas the first disappears after 11 hours, and the second after a further 17 hours heating, the third atom requires 63 hours; the temperature has to be considerably raised before the remaining atoms are driven off.

The second series of experiments was carried out in a similar manner, more care being taken to exclude moisture, which has apparently a notable influence on the rate of decomposition of the substance; the results are much more regular than in the first case, this being probably due to the absence of moisture.

The substance, $Ag_7NO_{11}$, may be regarded as a molecular combination of silver peroxide, $Ag_2O_2$, and a silver dioxynitrate of the composition $AgNO_5$, which gives a formula $3Ag_2O_2,AgNO_5$; this is not at variance with the valencies ordinarily ascribed to its constituent elements, but presupposes the existence of the salt of an acid, $HNO_5$, a substance not known at present. In general, the stability of a substance containing a large number of oxygen atoms decreases with increase in oxygen, so that the spontaneous decomposition of the substance $Ag_7NO_{11}$ would be explained by the presence of the dioxynitrate $AgNO_5$. The initial decomposition may be therefore expressed by the equation $3Ag_2O_2,AgNO_5 = 3Ag_2O_2,AgNO_3 + 2O$.

If, after elimination of two oxygen atoms, the residue is treated with water, an amount of silver nitrate is extracted corresponding with 17·8 per cent. of the original substance; the formula $3Ag_2O_2,AgNO_5$ requires 17·98 per cent. After the silver nitrate has been removed, the residue is found to resemble graphite in appearance, is comparatively stable, and has the formula $Ag_2O,5Ag_2O_2$, but is in all probability a mixture of the ordinary oxide and a silver peroxide, which does not resemble the one described by Berthelot, nor has it a red colour like that described by Iles (*Eng. and Min. Journ.*, 1884, 297). The presence of the ordinary oxide of silver may be explained by supposing that the initial decomposition already mentioned is accompanied by a secondary one, namely, the action of the oxygen liberated from the peroxynitrate on the silver peroxide, according to the equation $AgNO_5,3Ag_2O_2 = AgNO_3 + 2Ag_2O + Ag_2O_2 + 2O_2$.

On heating the peroxide, silver oxide, $Ag_2O$, is left, which has also the appearance of graphite, and is more stable than the ordinary variety of this oxide, not being decomposed below a temperature of 300°.

The author speculates on the possible existence of acids such as $HNO_5$ and $HNO_4$, and their corresponding anhydrides, $N_2O_5$ and $N_2O_4$.

A. W. C.

**Precipitated Calcium Carbonate.** By MAX ADLER (*Zeit. angw. Chem.*, 1897, 14, 431—434).—The precipitation of calcium carbonate in the aragonite form is determined by the temperature of the solutions, the concentration, the nature of the atmosphere in which the precipitation takes place, and by the pressure. In the preparation of calcium carbonate from solutions of calcium chloride and ammonium carbonate, the temperature at which the aragonite form is converted into the calcite form is increased to a much greater extent by an increase in the concentration of the ammonium carbonate than by an increase in the concentration of the calcium chloride. Using the ammonium carbonate of such a concentration that on adding the calcium chloride

a thick, gelatinous mass is obtained, the limit of temperature for the ammonium carbonate solution is 32°, whilst the calcium chloride may be used boiling. With dilute solutions at the same temperature, the aragonite crystals are at once converted into calcite; the limit of temperature for weak solutions is 22°, and the lower the temperature the smaller and more stable are the crystals of aragonite. The presence of carbonic anhydride in the solution determines the formation of calcite, and this explains the formation of calcite when the ammonium carbonate is at a high temperature, as it is then decomposed, with the formation of carbonic anhydride. Precipitated aragonite, when subjected to a pressure of 5—6 atmospheres, is converted into calcite. The aragonite form is more stable when the solution is alkaline with an excess of ammonium carbonate, and also when the precipitate is washed with water containing calcium sulphate instead of with pure water. When the aragonite prepared from calcium chloride and ammonium carbonate is separated from the mother liquor and heated to 60°, it is converted into calcite; on the other hand, the aragonite precipitated by sodium carbonate can be heated to 100° without change. E. C. R.

**Action of Cupric Hydroxide on Silver Nitrate Solutions.** By Paul Sabatier (*Compt. rend.*, 1897, **125**, 175—178).—When silver oxide is placed in a solution of an excess of cupric nitrate, the greenish-blue precipitate that forms is not copper hydroxide, as has hitherto been supposed, but is a basic cupric nitrate, $Cu(NO_3)_2,3Cu(OH)_2$. All the silver is dissolved in the form of nitrate. When the silver oxide and cupric nitrate are in equal molecular proportions, the product is a mixed basic nitrate of silver and copper, $3CuO,2AgNO_3,3H_2O$. When the silver oxide is in excess, the same product is obtained mixed with unaltered oxide.

When blue cupric hydroxide is added to silver nitrate solution, the mixed basic nitrate is obtained in microscopic needles. Neither cupric oxide nor the hydroxide $Cu_4H_2O_5$ (this vol., ii, 491) has any action on the silver nitrate solution, and if the blue hydroxide is mixed with either of them, the brown compound remains unchanged and is readily separated from the basic salt by levigation.

The basic silver copper nitrate forms blue-violet prisms, highly elongated and terminated by a base normal to the edges, or by a strongly inclined face. It is stable in dry air, but when heated loses water and decomposes into cupric oxide and silver nitrate. Hot water decomposes it at once into brown cupric hydroxide and silver nitrate, and cold water very slowly produces the same change. Cupric nitrate solution converts it into basic cupric nitrate, and the silver nitrate is dissolved. The double basic salt may be regarded as the compound $Cu(NO_3)_2,3CuO$, in which 1 atom of copper has been displaced by 2 atoms of silver, but the two basic salts are far from being isomorphous. C. H. B.

**Preparation of Thallium by Electrolysis.** By Fritz Foerster (*Zeit. anorg. Chem.*, 1897, **15**, 71—74).—Thallium chloride is prepared from the flue-dust of pyrites burners by precipitating the aqueous solution of the flue-dust with salt, then reconverting the product into sul-

phate and again precipitating with salt, the chloride thus obtained being heated with double the quantity of sulphuric acid necessary to convert it into the normal sulphate until copious acid fumes are given off. A saturated solution of the cold product is employed for the electrolysis. If too small an excess of sulphuric acid is present, brown thallium sesquioxide is deposited at the anode owing to the hydrolysis of thallium sulphate. The cathode consists of a circular ring of thin copper plate lying on the bottom of the glass vessel containing the electrolyte, two anodes of platinum foil being supported above it; in order to prevent short circuiting, the electrolyte is stirred by means of a glass stirrer which revolves between the anode and cathode and is driven by a fan. The stirring apparatus is similar to that employed in Ostwald's thermostat. A current density of 1·3—1·5 ampère per square decimetre and a potential difference of 3·5 volts. is employed; 30—50 grams of thallium chloride are then electrolysed in about 3 hours. The deposit of thallium is washed with water, dried by pressing between filter paper, and fused under potassium cyanide. The metallic regulus is preserved in a sealed tube under a solution of thallium hydroxide. It does not contain any recognisable quantities of lead or arsenic. E. C. R.

**Compounds of Hydrazine with Mercury Salts.** By KARL A. HOFMANN and E. C. MARBURG (*Ber.*, 1897, **30**, 2019—2022).—The authors have prepared several hydrazine derivatives of mercury salts which are, in their opinion, analogous to the well-known mercuriammonium compounds. When mercuric chloride and hydrazine hydrate are brought together in solution in alcohol and ether, a compound of the formula $N_2H_4HgCl_2$ is precipitated; it is moderately stable when dry, but unstable when moist, and decomposes rapidly when heated, but does not explode. When this compound is shaken with water, or when sodium acetate is added to the mixed aqueous solutions of hydrazine sulphate and mercuric chloride, an unstable yellow compound, $N_2H_2Hg_2Cl_2$, is produced which explodes when heated or struck, and rapidly decomposes when moist, nitrogen being evolved and mercury and calomel left. It is readily soluble in hydrochloric acid, but always leaves a small residue of calomel. Alkalis decompose it rapidly. These two compounds appear to be strictly analogous to the fusible and infusible white precipitates, $2NH_3,HgCl_2$ and $NH_2HgCl$.

Somewhat similar compounds have also been obtained from mercuric nitrate. The substance $N_2H_4Hg(NO_3)_2$ is formed as a curdy precipitate when hydrazine nitrate and mercuric nitrate are mixed in aqueous solution; it is not explosive, dissolves in acids, and is decomposed by alkalis with evolution of nitrogen. When hydrazine nitrate reacts with mercurous nitrate in aqueous solution, an amorphous, white precipitate is produced, which consists of the compound $N_2H_4Hg_2(NO_3)_2$; in pure water, it rapidly decomposes with separation of mercury, and it does not explode when heated. This is the only known ammoniacal derivative of a mercurous salt, the others which have been described having been proved to be mixtures of mercury with the corresponding mercuric derivative. A. H.

**Condition in which Elements other than Carbon exist in Iron and Steel.** By ADOLPHE CARNOT and GOUTAL (*Compt. rend.*, 1897, **125**, 148—152, and 213—216).—When iron is dissolved in dilute hydrochloric acid out of contact with air, the greater part of the silicon is left undissolved in the form of an iron silicide, FeSi. The remainder of the silicon is converted into the hydroxide, $SiO(OH)_2$, and seems to exist in the iron in the form of silicides intermediate between $Fe_3Si_2$ and $Fe_5Si_2$. When the iron contains manganese, practically the whole of the latter is found in combination with the silicon in the insoluble residue, and it would seem to follow that silicon combines with manganese in preference to combining with iron.

When iron and steel are heated with dilute acids, almost all the sulphur is converted into hydrogen sulphide, but when the solvent is a neutral or faintly acid solution of cupric potassium chloride, all the sulphur remains in the insoluble residue, partly as iron sulphide, but often mainly as cupric sulphide. Direct experiment shows that the copper solution has no action on ferrous sulphide, and it follows that the suphur is partly present in the metal in the form of some other sulphide. Direct experiment shows that the sulphur in combination with copper in the residue is equivalent to the manganese present in the iron or steel, and hence it would seem that part of the sulphur exists in the iron or steel in the form of manganese sulphide, MnS, and that, at high temperatures, sulphur combines with manganese in preference to iron, a conclusion which agrees with the known use of spiegeleisen or ferromanganese for eliminating sulphur from cast-iron.

When the solvent is neutral cupric potassium chloride solution, all the phosphorus is found in the residue in the form of iron phosphide, $Fe_3P$, identical with that described by Schneider; arsenic, on the other hand, is completely dissolved by the copper solution, but if the solvent is dilute hydrochloric acid, and air is excluded, all the arsenic remains as such in the residue, and presumably exists uncombined in the metal, mixed with or dissolved in the iron.

Manganese, when in small quantity, is present in the form of silicide or sulphide, but when in larger quantity, part of it is either dissolved in or is combined with the iron, and the method of examination adopted is unable to determine the exact condition.

Copper is found as such in the residue left when the iron or steel is dissolved in dilute acids out of contact with air. Titanium behaves similarly with either solvent. It follows that copper and titanium both exist as such in the iron or steel.

Nickel is partially attacked by dilute acids, even out of contact with air, but the nickel left in the residue is in the metallic state, and is free from iron. Probably, therefore, it is simply mixed with or dissolved in the iron.

Chrome-steels are readily attacked by acids if they are highly carburetted, but not otherwise, and the composition of the residues indicates that the chromium is present in the form of chromium-iron carbides.

Tungsten is left undissolved by dilute acids, in the form of the compound $Fe_3W$, and molybdenum is left in the form of the compound $Fe_3Mo_2$. Both these compounds, therefore, exist in the iron or steel.

C. H. B.

**Chromium.** By Henri Moissan (*Ann. Chim. Phys.*, 1896, [vii], 8, 559—570).—The preparation of pure chromium is fully described and its chief properties given (Abstr., 1893, ii, 281; 1894, ii, 452).

A. C. C.

**Arsenothiomolybdates.** By Rudolph F. Weinland and Karl Sommer (*Zeit. anorg. Chem.*, 1897, 15, 42—65).—*Sodium pyrothioarsenothiomolybdate*, $As_2S_7(MoS_3)_2Na_4 + 14H_2O$, is obtained by adding molybdenum trisulphide (2 mols.) to a solution of sodium thioarsenate (1 mol.) heated on the water bath; a portion of the trisulphide remains undissolved, and a brown bye-product is also formed. The filtrate, on evaporation, yields the salt mixed with the brown, amorphous bye-product, which, although insoluble in water, is easily soluble in a solution of the salt; the two are most conveniently separated by dissolving the crude salt in a large quantity of ice-cold water, when the brown bye-product remains for the most part undissolved. The salt is also formed on boiling a solution of sodium pyrothioarsenate with molybdenum trisulphide, but large quantities of bye-products are formed at the same time. It can, however, be easily obtained in a pure state by adding salicylic acid (1 mol.) to a solution of molybdenum trisulphide (1 mol.) in sodium thioarsenate (1 mol.), and precipitating the clear filtrate with alcohol. It crystallises in lustrous, dark red, six-sided prisms, gradually decomposes when dry, and is then no longer entirely soluble in water, is not hygroscopic, and loses its water of crystallisation at 105°. It is decomposed by dilute mineral acids with evolution of hydrogen sulphide and precipitation of a reddish-brown sulphide, and gives characteristic coloured precipitates with solutions of metallic salts. This salt is also produced by the action of arsenic pentasulphide on sodium thiomolybdate. The *potassium* salt, with $8H_2O$, which can be prepared in a similar manner to the sodium salt, crystallises in bright red, slender needles, is easily soluble in water, insoluble in alcohol, and has properties like those of the sodium salt. The *ammonium* salt, with $5H_2O$, is best prepared by adding salicylic acid (4 mols.) to a concentrated solution of ammonium pyrothioarsenate and ammonium thiomolybdate, and then precipitating with alcohol; it crystallises in slender, scarlet needles, is very unstable, and cannot be obtained pure. The aqueous solution quickly decomposes with evolution of ammonia and hydrogen sulphide. The *barium* salt, with $14H_2O$, is obtained by dissolving arsenic pentasulphide in a solution of barium thiomolybdate, and cooling the filtrate to $-15°$. It cannot be obtained by the action of molybdenum trisulphide on barium thioarsenate, as under these conditions sulphur is precipitated, and a double salt of barium thioarsenate and barium thioarsenite is formed. It crystallises in slender, red needles, and when recrystallised partially decomposes with separation of sulphur.

*Sodium metathioarsenothiomolybdate*, $AsS_3(MoS_3)Na + 6H_2O$, is obtained by treating the above sodium pyrothioarsenothiomolybdate with salicylic acid ($1\frac{1}{2}$ mol.) and a small quantity of water at 40—50°. The clear solution is precipitated with alcohol, and the precipitate washed with dilute alcohol and then with sufficient cold water to extract the

sodium salicylate and undecomposed pyrosalt. It is an amorphous, cherry-red powder, insoluble in water, and easily soluble in dilute sodium hydroxide and ammonia. The *potassium* salt, with $4H_2O$, obtained in a similar manner to the sodium salt, is an amorphous, red powder.

*Potassium pyrothioarseno-oxythiomolybdate*, $As_2S_7(Mo_2S_3O_3)K_4 + 6H_2O$, is obtained by boiling arsenic pentasulphide (1 mol.) with a solution of molybdenum trisulphide (2 mols.) in potassium hydroxide (4 mols.). On concentrating the solution, potassium pyrothioarsenothiomolybdate first crystallises out, and on further concentrating the mother liquors the salt separates in slender needles; it is also formed by the action of arsenic pentasulphide on a solution of molybdic acid in potassium hydrogen sulphide. It crystallises in yellow, slender, six-sided needles, is very easily soluble in water, and when the solution is treated with acetic acid it gradually becomes dark red; this reaction is characteristic of the oxythiomolybdates. With hydrochloric acid, it gives a yellowish-brown precipitate, also characteristic precipitates with solutions of the salts of the heavy metals. The salt with $10H_2O$, obtained by boiling a solution of potassium thiomolybdate with dipotassium arsenate, crystallises in yellow needles. The *sodium* salt, with $15H_2O$, is obtained by boiling ammonium thiomolybdate (2 mols.) with sodium hydroxide (4 mols.) until all the ammonium sulphide is driven off, and then adding arsenic pentasulphide, and boiling until the latter is dissolved. Metathioarseno-oxythiomolybdate, which is also formed during the reaction, crystallises out first, and the salt is obtained on concentrating the mother liquors. It crystallises in slender, yellow needles, and resembles the potassium salt. The *magnesium* salt, with $16H_2O$, prepared in a similar manner to the sodium salt, crystallises in slender, yellow needles, and the *barium* salt, with $12H_2O$, in slender, yellow needles.

*Potassium metathioarseno-oxythiomolybdate*, $AsS_3(MoO_2S)K + 2\frac{1}{2}H_2O$, obtained as a bye-product in the preparation of the preceding potassium salt from arsenic pentasulphide, molybdic acid, and potassium hydrogen sulphide, is a fine, orange-red powder, which partially decomposes when recrystallised; when treated with hydrochloric acid, all the arsenic and molybdenum are precipitated as a reddish-yellow powder, but the colour of the solution is not altered by acetic acid. With ammonium, barium, strontium, and calcium salts, it gives yellow, amorphous precipitates which are insoluble in cold water, and with salts of the heavy metals, it yields characteristic precipitates. When heated in a tube, sulphurous anhydride is given off; this decomposition takes place slowly at 100°, so that the determination of the water of crystallisation must be effected at 90°. The *sodium* salt, with $5H_2O$, is lemon-yellow when freshly prepared, and becomes reddish-yellow on recrystallisation; it resembles the potassium salt.

E. C. R.

**Hydroxylamine-ammonia Compounds of Uranic Acid.** By KARL A. HOFMANN (*Zeit. anorg. Chem.*, 1897, **15**, 75—80).—*Hydroxylamine ammoniouranate*, $UO_4(NH_3OH)_2,2NH_3$, is obtained by adding ammonia (7 per cent. 100 c.c.) to an aqueous solution of uranyl

nitrate (20 grams) and hydroxylamine hydrochloride (10 grams). The product, after being washed with dilute ammonia, alcohol, and ether, and dried at the ordinary temperature, is a lustrous, canary-yellow, crystalline powder consisting of microscopic, rhombic tablets; it is stable at the ordinary temperature, loses ammonia when heated at 73°, and decomposes with a slight explosion when heated to 178—180° in a capillary tube. It reduces Fehling's solution at the ordinary temperature, and when cautiously heated to 120° is converted into uranic acid, $UO_4H_2$.

*Hydroxylamine uranate*, $UO_4(NH_4O)_2 + H_2O$, can be obtained by heating the preceding compound with glycerol at 100°, by allowing it to remain with water at the ordinary temperature for some hours, or by treating it with hot water; it is also obtained when uranic acid or uranyl nitrate is digested with excess of an aqueous solution of hydroxylamine. It crystallises in yellow, elongated plates pointed at both ends at an angle of 126°. When heated, it decomposes with a slight explosion, yielding a greenish-black powder. It reduces Fehling solution with great ease.

Hydroxylamine ammonio-uranate, when treated with 2 mols. of acetic acid, yields ammonium acetate and hydroxylamine uranate; with excess of acetic acid, it yields a double salt of uranyl acetate and hydroxylamine acetate which crystallises in yellow, lustrous prisms.

E. C. R.

**Zirconium Tetriodide.** By LOUIS M. DENNIS and A. E. SPENCER (*J. Amer. Chem. Soc.*, 1896, **18**, 673—679).—Attempts to obtain this compound by passing iodine vapour over zirconium heated to dull redness in a current of hydrogen met with no success. It was, however, eventually obtained by passing hydrogen iodide, prepared by Merz and Holzmann's method (Abstr., 1889, 754) over zirconium. As the tube containing the latter was gradually heated, an amorphous, white sublimate, probably of ferrous iodide obtained from traces of iron in the metal, first formed, and finally, at a bright red heat, a white, crystalline sublimate was deposited immediately beyond the red hot portion of the tube. After cooling in a current of hydrogen, the zirconium was found to have changed from black to greyish-white, but contained very little iodine. The composition of the crystalline sublimate, which consists of colourless cubes exhibiting no double refraction, proved on analysis to correspond with the formula $ZrI_4$. It is insoluble in water, nitric acid, hydrochloric acid, aqua regia, and carbon bisulphide, but decomposed and dissolved by concentrated sulphuric acid and partially decomposed by concentrated nitric acid with liberation of iodine and formation of a white powder insoluble in nitric acid but soluble in concentrated sulphuric acid. On heating in hydrogen, the iodide turns black, and iodine and hydriodic acid are formed, and on heating in the air it melts and sublimes. The iodide is unchanged by boiling with water, in this respect resembling Deville's fluoride, but differing from the deliquescent, easily decomposable tetrachloride and tetrabromide. E. W. W.

**Double Fluorides of Zirconium with Lithium, Sodium, and Thallium.** By HORACE L. WELLS and H. W. FOOTE (*Amer. J. Sci.*,

1897, 3, 466—471).—Thallium fluoride was prepared by dissolving the metal in sulphuric acid, adding an excess of baryta water, filtering, and passing carbonic anhydride into the hot solution; the filtrate was then evaporated and treated with excess of hydrofluoric acid. The salts were prepared by mixing the acid fluorides in varying proportions, evaporating and cooling to crystallisation. In all cases they are stable in the air.

The *salt* $2LiF,ZrF_4$, formed when 0·7—2 grams of lithium fluoride is added to 20 grams of zirconium fluoride, crystallises in hexagonal prisms very similar to the crystals of quartz found in Herkimer Co., N.Y.; when recrystallised, it is converted into the 4:1 salt. The *salt* $4LiF,ZrF_4 + \frac{2}{3}H_2O$, obtained when 5—7 grams of lithium fluoride is added to 20 grams of zirconium fluoride, is somewhat difficult to prepare owing to the insolubility of lithium fluoride; it separates in crystalline crusts. On recrystallising, lithium fluoride is precipitated.

The *salt* $2NaF,ZrF_4$ is prepared by adding 2 parts of sodium fluoride to 14 parts of zirconium fluoride; it separates in crusts of minute, hexagonal crystals and cannot be recrystallised. The *salt* $5NaF,2ZrF_4$, previously described by Marignac, is formed under very wide conditions; it crystallises in thick, orthorhombic prisms.

The *salts* $TlF,ZrF_4$ and $TlF,ZrF_4 + H_2O$ are obtained when 1 part of thallium fluoride is mixed with 3—4 parts of zirconium fluoride; the hydrated salt crystallises in needles if the solution is cooled before precipitation occurs, but if the solution is evaporated until crystals begin to form and is then cooled, the anhydrous salt separates in minute, square plates. When recrystallised, it is converted into the 5:3 salt. The *salt* $5TlF,3ZrF_4$, is prepared by mixing 1—3·5 parts of thallium fluoride with 1 part of zirconium fluoride; it crystallises in needles. When, however, 4 parts of thallium fluoride are employed, the same salt is produced, but it crystallises in hexagonal prisms. Both modifications, when recrystallised, separate in needles. The *salt* $3TlF,ZrF_4$ is obtained when 1 part of zirconium fluoride is added to 4—20 parts of thallium fluoride; it crystallises in brilliant octahedra and can easily be recrystallised. E. C. R.

## Mineralogical Chemistry.

**Argentiferous Gold from Lower California.** By CARLOS F. DE LANDERO (*Mem. Soc. Cient. "Antonio Alzate," Mexico*, 1896, 10, 75—77).—Rounded grains of gold of a pale yellow colour, from the placers at Alamo, district Norte del Territorio, Lower California, gave on analysis,

| Au. | Ag. | Quartz sand. | Total. |
|---|---|---|---|
| 80·58 | 17·22 | 1·39 | 99·19. |

This corresponds with $Au_5Ag_2$. Specimens of electrum from Colombia and the Urals have nearly the same composition.

L. J. S.

**Arsenic Compounds of Iron, Nickel and Cobalt.** By CARL FRIEDRICH RAMMELSBERG (*Jahrb. f. Min.*, 1897, ii, 45—66).—Löllingite, mispickel, niccolite, rammelsbergite, smaltite, chloanthite, gersdorffite, cobaltite, skutterudite &c., the cubic, orthorhombic and rhombohedral arsenides and antimonides of iron, nickel and cobalt, may all be represented by the general formulæ $RS_2,xR_m(As,Sb)_n$. Here $m : n$ varies from 1 : 1 (in niccolite) to 1 : 3 (in skutterudite), and between these limits there can be variations without alteration of crystal form; the various ratios of $R_m : As_n$ must therefore be considered as forming isomorphous mixtures. Similar cases of variation of composition without effect on the crystal form is shown by artificial alloys containing arsenic or antimony, and in the mineral dyscrasite. The sulphur of the isomorphous portion $RS_2$, gradually increases in amount from zero until $x = 1$.

Numerous analyses of these minerals are discussed in detail, and special formulæ given to suit the various cases. For löllingite are given, $Fe_3As_4$ (leucopyrite), $FeS_2,4Fe_2S_3$; $2FeS_2,3Fe_5As_8$; $3FeS_2,Fe_3As_5$, &c. Mispickel, which is generally $FeS_2,FeAs_2$, is also represented by $5FeS_2,Fe_6As_{11}$; $8FeS_2,7FeAs_2$, &c., in order to explain the variations shown by the sulphur. In the nickel and cobalt compounds, the ratios taken for $m : n$ are, 1 : 1, 1 : 1·33, 1 : 1·5, 1 : 1·66, 1 : 2, 1 : 2·5, and 1 : 3; whilst $x$ varies considerably, for example, in passing from smaltite to cobaltite. L. J. S.

**Composition of Nagyagite.** By EDUARD PŘIWOZNIK (*Chem. Centr.*, 1897, ii, 54; from *Österr. Zeit. Berg-Hütt.*, 1897, 45, 265—267).—The composition of nagyagite is doubtful; the present analysis leads to the formula $Te_6Pb_6AuS_8 = 4PbS,2PbTe,AuTe_2 + 2TeS_2$.

| Te. | S. | Au. | Pb. | Total. |
|---|---|---|---|---|
| 29·88 | 10·73 | 8·11 | 51·18 | 100·00. |

L. J. S.

**Formation of Cuprite by Electrolysis of Copper Sulphate Solution.** By QUIRINO MAJORANA (*Rend. Accad. Linc.*, 1895, 4, i, 371—375).—Small crystals of cuprite are formed on electrolysing a saturated neutral solution of copper sulphate at the ordinary temperature, using a very small current density; as the solution becomes acid by continued electrolysis, crystals of metallic copper make their appearance, and if the solution is acid to start with, no cuprite crystals are formed. The author finds also that the quantity of free acid necessary to prevent the formation of cuprite crystals is less in proportion as the current density is greater. W. J. P.

**Formation of Bauxite and allied Minerals.** By A. LIEBRICH (*Zeits. prakt. Geol.*, 1897, 212—214. Compare this vol., ii, 104).—Alumina is not liberated from silicates by the ordinary weathering agencies; it is therefore, in its various combinations (hydrates, sulphates, aluminates), of much less common occurrence than the easily liberated oxides of iron. The action of sulphuric acid, derived from pyrites or hydrogen sulphide, on aluminium silicates would give rise to solutions of aluminium sulphate, from which the various mineral sulphates or hydrates (bauxite, &c.) could be deposited. Sulphuric

acid in contact with fluorides gives hydrogen fluoride, which, in acting on aluminium silicates, would give aluminium fluorides (cryolite, &c.). It is suggested that aluminates (spinel, $MgO,Al_2O_3$, for example) may have been formed by the loss of sulphuric acid and water from the corresponding double sulphates; for example, pickeringite,

$$MgO,Al_2O_3,(SO_3)_4 + 22H_2O.$$

L. J. S.

**Fluorite from Argentina.** By JEAN VALENTIN (*Zeit. prakt. Geol.*, 1896, 104—107).—Coarsely crystalline fluorite occurs in veins at the granite-gneiss contact, 20 kilometres south of San Roque, prov. Cordoba. It is accompanied by quartz and a little pyrites. Several analyses are given, the amount of calcium fluoride varying from 84·20 to 98·12 per cent.; the purest gave

| | $CaF_2$. | $Al_2O_3 + Fe_2O_3$. | MgO. | $SiO_2$. |
|---|---|---|---|---|
| Dark blue, almost black ... | 96·59 | 1·20 | trace | 2·08 |
| Greenish .................... | 97·03 | 2·52 | ,, | trace |
| Greenish-white ............. | 98·12 | 1·68 | ,, | ,, |

Blue or violet fluorite occurs with galena, cassiterite, &c., in the wolframite and molybdenite veins of the Sierra de Cordoba. Previously this mineral had only been known to occur in Argentina in small amount.

L. J. S.

**Occurrence of Iodine in Malachite.** By WILHELM AUTENRIETH (*Zeit. physiol. Chem.*, 1897, 22, 508—513).—Examination of a specimen of malachite, of unknown locality, showed that it contained both iodine and chlorine, the amount of halogen varying, in the case of iodine, from 0·08—0·4 per cent., and in that of chlorine from 1·8—5·5 per cent. The same mineral also contained traces of iron, calcium, magnesium, and several per cent. of a residue insoluble in hydrochloric acid. The author has further examined a large number of malachites from known localities, also atacamite and azurite, without, in any single instance, being able to detect even traces of iodine. In all probability, the mineral examined was a specimen of Chilian atlasite, which is known to contain as much as 8 per cent. of copper chloride.

A. W. C.

**Formula of Apatite.** By CARL F. RAMMELSBERG (*Jahrb. f. Min.*, 1897, ii, 38—44).—The ratio $(F + Cl) : P = 1 : 3$, required by the well-known apatite formula $3Ca_3P_2O_8 + Ca(F,Cl)_2$ ("normal apatite"), although supported by several later analyses, does not always hold good. In the latter case, the formula must be written as $3Ca_3P_2O_8 + Ca(F_2,O)$, since there is a slight excess of calcium over that required to combine with the phosphoric acid and fluorine. Several recent analyses by Carnot (Abstr., 1896, ii, 611) are of this kind; his analysis of apatite from Greiner, in the Zillerthal, with only 0·37 per cent. fluorine, corresponds with $3Ca_3P_2O_8 + Ca(O_{11/12},F_{2\,1/12})$. Völker's analysis (1858) of apatite from Kragerö, with 4·20 per cent. chlorine and no fluorine, corresponds with $3Ca_3P_2O_8 + Ca(O_{2/5},Cl_{2\,3/5})$; Laspeyres finds only a trace of fluorine in this apatite.

The question arises whether apatites which are poor in fluorine are of original formation, or have been derived by the alteration of normal apatite, fluorine having been abstracted, and a basic phosphate

formed. The latter is here considered to be the more probable, since CaO and $CaF_2$ are not isomorphous, and, further, apatite is easily altered by the action of waters into phosphorite, pseudoapatite, &c. This view is supported by the fact that many of Carnot's analyses show the presence of impurities. L. J. S.

**A Basic Sulphate of Copper.** By GIUSEPPPE CESÀRO and H. BUTTGENBACH (*Ann. Soc. Geol. Belgique*, 1897, **24**, *Bull.*, pp. xli—xliii).—The specimen described, which is probably from Nassau, is a compact green mass of small crystals. Microscopical examination shows the crystals to be orthorhombic and apparently hemimorphic; they are flattened parallel to the perfect pinacoidal cleavage. The acute positive bisectrix is parallel to this cleavage. Analyses lead to the formula $CuSO_4,2Cu(OH)_2$. This, which seems to be a new mineral, differs from brochantite, $CuSO_4,3Cu(OH)_2$, in its optical characters. Friedel has prepared a basic copper sulphate having the composition $CuSO_4,2Cu(OH)_2$. L. J. S.

**Constitution and Classification of Sulpharsenites, &c.** By VASILE C. BUTUREANU (*Bul. Soc. Sci. Bucarest*, 1897, **6**, 172—182).—Several of the hypothetical thio-acids of the general formula $m(AsS_3H_3) - nSH_2$ are expressed graphically, and the corresponding structural formulæ are given for all the known mineral sulpharsenites, sulphantimonites and sulphobismuthites. Stephanite, polybasite, and polyargyrite cannot be written graphically as basic salts of the ortho-acid ($SbS_3H_3$), they are accordingly supposed to be tetrabasic diortho-sulphantimonites ($Sb_2S_5Ag_4$) with an excess of silver sulphide. L. J. S.

**Analyses of Serpentines.** By GINO TURI (*Gazzetta*, 1897, **27**, ii, 82—86).—The author has analysed serpentines from the locality dell' Impruneta near Florence; the serpentine is of two kinds, white and green, and was separated before analysis. The accompanying table gives the analytical results; A and B refer to samples from the Black Rock Hill (Poggio dei Sassi Neri) and C and D are from the Mine dell' Impruneta (Miniera dell' Impruneta).

| | A. | | B. | | C. | | D. | |
|---|---|---|---|---|---|---|---|---|
| | White. | Green. | White. | Green. | White. | Green. | White. | Green. |
| $H_2O$ | 13·40 | 12·65 | 13·70 | 12·80 | 13·02 | 12·06 | 12·85 | 11·70 |
| $SiO_2$ | 42·00 | 39·55 | 42·80 | 43·87 | 41·04 | 42·56 | 40·92 | 42·12 |
| FeO | 2·30 | 6·49 | 3·42 | 2·45 | 1·53 | 3·02 | 2·45 | 4·80 |
| $Fe_2O_3$ | 5·75 | 7·86 | 5·09 | 10·75 | 4·60 | 8·34 | 4·32 | 7·05 |
| MgO | 36·40 | 32·53 | 33.94 | 29·36 | 39·03 | 33·60 | 39·05 | 33·15 |
| $Cr_2O_3$ | 0·00 | 0·00 | 0·00 | 0·00 | 0·00 | 0·20 | 0·00 | 0·28 |
| Total | 99·85 | 99·08 | 98·95 | 99·23 | 99·22 | 99·78 | 99·59 | 99·10 |

The serpentines also contain traces of calcium and sodium.

W. J. P.

**Rœblingite, a New Silicate from Franklin Furnace.** By SAMUEL L. PENFIELD and H. W. FOOTE (*Amer. J. Sci.*, 1897, [iv], 3, 413—415; and *Zeits. Kryst. Min.*, 1897, 28, 578).—Rœblingite occurs as dense, white, compact masses filling cavities in axinite which forms veins in the garnet rock of the zinc deposits of Franklin, New Jersey. Under the microscope, it is seen to consist of an aggregate of minute, prismatic crystals with parallel extinction and weak double refraction. The hardness is a little below 3; sp. gr. 3·433. The powdered mineral is easily soluble in dilute acids, with separation of gelatinous silica and evolution of sulphurous anhydride. The mean of two very similar analyses by Foote is

| $SiO_2$. | $SO_2$. | PbO. | MnO. | CaO. | SrO. | $K_2O$. | $Na_2O$. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|---|---|---|
| 23·58 | 9·00 | 31·03 | 2·48 | 25·95 | 1·40 | 0·13 | 0·40 | 6·35 | 100·32 |

This gives the molecular ratios as $SiO_2 : SO_2 : PbO : (Ca, Mn, Na_2, \&c.\ O) : H_2O = 5·61 : 2·01 : 1·99 : 7·43 : 5·04$, from which the formula is given doubtfully as $H_{10}Ca_7Pb_2Si_5S_2O_{28} = 5H_2CaSiO_4 + 2(CaO,PbSO_3)$. As the water can only be driven off at a rather high temperature, it is to be regarded as hydroxyl. It is not probable that the mineral is a mixture or contains much foreign material, and is the first naturally occurring sulphite that has been observed. The name is given after W. A. Rœbling.

L. J. S.

**Monoclinic Pyroxenes of New York State.** By HEINRICH RIES (*Jahrb. f. Min.*, 1897, ii, Ref. 26—28; from *Ann. N.Y. Acad. Sci.*, 1896, 9, 126—178).—In this monograph, detailed descriptions are given of all the known occurrences of monoclinic pyroxenes (except wollastonite) in the State of New York. They occur in gneisses and gabbros, in contact- and dynamo-metamorphic limestones, and in magnetite. The lighter coloured varieties are found in the dynamo-metamorphic limestones, and the darker in the contact-limestones; those from the magnetite are almost opaque in thin sections. On the crystals, 16 forms are noted; the habit of each occurrence is very characteristic. Tschermak's assertion that Ca is always greater than Mg + Fe, does not hold good for these aluminous pyroxenes. The darker pyroxenes are usually altered to uralite, and the lighter to tremolite, other decomposition products being serpentine, chlorite, rose-red garnet, and clintonite. The following analyses are given.

| | $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | CaO. | MgO. | Alkalis. | Loss on ignition. | Total. | sp. gr. |
|---|---|---|---|---|---|---|---|---|---|---|
| I. | 54·63 | 5·26 | — | 3·00 | 22·63 | 14·18 | — | — | 99·70 | — |
| II. | 53·97 | 4·94 | 0·50 | 8·63 | 23·96 | 7·32 | — | — | 99·32 | 3·36 |
| III. | 56·00 | 8·44 | 4·70 | 2·40 | 21·63 | 5·23 | 0·50 | 0·20 | 99·10 | 3·5 |
| IV. | 56·14 | 8·19 | 0·38 | 2·85 | 17·79 | 13·67 | — | — | 99·02 | — |
| V. | 46·28 | 7·38 | 2·21 | 14·80 | 18·78 | 8·91 | — | 1·115 | 100·065 | 3·386 |
| VI. | 54·57 | 3·09 | — | 1·30 | 21·42 | 18·56 | 0·40 | 0·15 | 99·49 | — |
| VII. | 49·12 | 7·49 | 3·53 | 15·98 | 17·30 | 6·06 | — | — | 99.48 | 3·60 |
| VIII. | 52·01 | 5·82 | 0·67 | 6·86 | 26·90 | 11·26 | 0·50 | — | 104·02 | 3·60 |
| IX. | 50·05 | 7·16 | 0·56 | — | 25·63 | 14·48 | — | 1·66 | 99·54 | 3·26 |
| X. | 53·30 | 4·11 | — | 0·80 | 24·82 | 16·18 | — | 0·15 | 99·36 | 3·18 |
| XI. | 54·86 | 0·75 | — | 1·30 | 24·13 | 18·14 | 0·35 | 0·10 | 99·63 | 3·29 |
| XII. | 54·57 | 1·12 | — | 1·80 | 23·25 | 17·78 | 0·70 | 0·38 | 99·60 | 3·27 |
| XIII. | 54·94 | 2·42 | — | 1·29 | 25·38 | 17·60 | 0·28 | — | 101·91 | 3·00 |

The following optical determinations (extinction angle $\mathfrak{c} : \mathfrak{c}$, &c.), show no definite relation to the amount of ferrous oxide present.

| | $\dot{c}:\mathfrak{c}$ | 2V | $\alpha$ | $\beta$ | $\gamma$ | $FeO + Fe_2O_3 + Al_2O_3$ |
|---|---|---|---|---|---|---|
| II. | 41° 30′ | 60° 40′ | 1·6888 | 1·6932 | 1·7108 | 14·07 |
| VI. | 41 30 | 59 40 | 1·6806 | 1·6843 | 1·7036(Na) | 4·39 |
| X. | 40 | 59 | 1·6778 | 1·6848 | 1·7025 „ | 4·91 |
| XI. | 40 | 59 30 (Na) | 1·6749 | 1·6852 | 1·7013 „ | 2·05 |
| XII. | 41 | 56 30 „ | 1·6683 | 1·6730 | 1·6902 „ | 2·92 |
| XIII. | 37 | 58 56 „ | 1·6626 | 1·6718 | 1·6940 „ | 3·71 |

Other optical determinations are also compared with the amount of $FeO + Fe_2O_3 + Al_2O_3$.

I. Granular, transparent, light grey, in calcite. Cascadeville, Essex Co.

II. Dark green crystals in contact limestone. Diana, Lewis Co.

III. Black crystals in calcite. Weston Magnetite mine, Keene, Essex Co.

IV. Dark green prismatic grains in limestone. Keene, Essex Co.

V. Diallage in gabbro. Mt. Marcy, Essex Co.

VI. Green crystals with microcline and albite. Pitcairn, St. Lawrence Co.

VII. Black, with magnetite. Port Henry, Essex Co.

VIII. Dark green crystals in scapolite in contact limestone. Warwick, Orange Co.

IX. Leucite-augite in grains with calcite and seybertite. Amity, Orange Co.

X. Light, transparent crystals in limestone. Sing-Sing, Westchester Co.

XI. Diopside. De Kalb, St. Lawrence Co.

XII. White, in limestone. Port Henry, Essex Co.

XIII. Green, glassy diopside. Russell, St. Lawrence Co.

L. J. S.

**Chabazite with Crystal-water Crystal-carbon-bisulphide, &c.** By Friedrich Rinne (*Jahrb. f. Min.*, 1897, ii, 28—37).—The fact, recently discovered by G. Friedel (Abstr., 1896, ii, 481), that dehydrated zeolites absorb ammonia and other gases, may be due to a mechanical condensation of the gas or to molecular action; in the latter case, there would be a corresponding change in the physical characters of the zeolite. In order to test this, the present author has made optical examinations of chabazite. A partially dehydrated crystal plate of the mineral when placed in liquid carbon bisulphide exhibits a gradual change in the extinction angles, and becomes more strongly birefringent; on heating the plate, the carbon bisulphide is expelled with a return to the original optical characters. The absorption of carbonic anhydride, alcohol, chloroform, benzene, or aniline is also accompanied by similar changes in the optical characters.

L. J. S.

**Meerschaum.** By R. Helmhacker (*Berg. u. huettenm. Zeit.*, 1897, 61, 44—46).—By surface agencies, serpentine is altered into an impure limonite, or, when not actually exposed, into a clay-like, crumbly mass consisting of opal, quartz, magnesite, gymnite and talc; when the earth-covering is of considerable thickness, nodules of meerschaum are

also formed. The associated opal and magnesite occur intimately intermixed with the meerschaum, which explains the variations in composition shown by analyses. Freshly obtained meerschaum is soft and dough-like and of a pale green colour; it is only on exposure to the air that it becomes hard and white. The occurrences of meerschaum in Moravia, Bosnia, and Asia Minor are described. The associated magnesite from Hrubšic, in Moravia, gave on analysis.

| $CO_2$. | MgO. | CaO. | $Al_2O_3,Fe_2O_3$. | $SiO_2$. | $P_2O_5$. | Total. |
|---|---|---|---|---|---|---|
| 51·60 | 46·10 | 1·45 | 0·81 | 0·60 | 0·24 | 100·80 |

L. J. S.

**Wellsite, a New Mineral.** By JULIUS H. PRATT and H. W. FOOTE (*Amer. Journ. Sci.*, 1897, [iv], 3, 443—448; and *Zeits. Kryst. Min.*, 1897, **28**, 581).—This new zeolite occurs with albite, hornblende and chabazite in a corundum vein at Buck Creek corundum mine, Clay Co., North Carolina. The small, isolated crystals are invariably interpenetration twins closely resembling those of phillipsite and harmotome, the twin planes being, as in these species, $c(001)$ and $e(011)$. The monosymmetric constants are given below. The crystals are colourless and transparent to white, with a vitreous lustre; they are brittle and possess no cleavage. H = 4—4·5; sp. gr. = 2·278—2·366. The acute, positive bisectrix is perpendicular to (010), and the optic axial angle is large. The mineral is decomposed by hot hydrochloric acid with separation of silica, but without gelatinisation. The mean of two analyses is,

| $SiO_2$. | $Al_2O_3$. | BaO. | SrO. | CaO. | MgO. | $K_2O$. | $Na_2O$. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|---|---|---|
| 43·86 | 24·96 | 5·07 | 1·15 | 5·80 | 0·62 | 3·40 | 1·80 | 13·35 | 100·01. |

This gives the formula $R''Al_2Si_3O_{10} + 3H_2O$, in which, approximately, $BaO : CaO : (K,Na)_2O = 1 : 3 : 2$. About one-third of the water is expelled between 100° and 200°, another third at 200—300°, and the remainder on ignition. After being heated to 265°, nearly all the water is regained from moist air. The close relation of the new mineral to the phillipsite group is shown by the following table.

| | | $a$ : $b$ : $c$ | $\beta$ |
|---|---|---|---|
| Wellsite, | $RAl_2Si_3O_{10} + 3H_2O$ ... | 0·768 : 1 : 1·245 | 53°27′ |
| Phillipsite, | $RAl_2Si_4O_{12} + 4\frac{1}{2}H_2O$... | 0·7095 : 1 : 1·2563 | 55 37 |
| Harmotome, | $RAl_2Si_5O_{14} + 5H_2O$ ... | 0·7032 : 1 : 1·2310 | 55 10 |
| Stilbite, | $RAl_2Si_6O_{16} + 6H_2O$ ... | 0·7623 : 1 : 1·1940 | 50 50 |

Here the ratios $RO : Al_2O_3$ and $SiO_2 : H_2O$ are constant, and = 1 : 1; phillipsite is, however, an exception to this, and it should therefore probably have only $4H_2O$. Another member of this series would be expected to be $RAl_2Si_2O_8 + 2H_2O$, this being related to the anorthite formula in the same way that stilbite is related to albite.

L. J. S.

**[Orthoclase, Melanite and Zircon from Alnö.]** By ARVID G. HÖGBOM (*Zeits. Kryst. Min.*, 1897, **28**, 506; from *Geol. För. i Stockholm Förh.*, 1895, **17**, 137, 145, 148).—In a paper on the geology and petrology of the nephelite-syenite district of the Island of Alnö, Sweden,

the following mineral analyses are given. Orthoclase, containing barium, I. Melanite, II; the $Fe_2O_3$ includes a little FeO. Zircon, III. (Analyses I and II are by N. Sahlbom; III by P. J. Holmquist).

| | $SiO_2$. | $ZrO_2$. | $TiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MnO. | CaO | $Na_2O$. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| I. | 62·10 | — | — | 19·46 | — | trace | — | 0·89 | 1·19 | 0·67 | |
| II. | 31·15 | — | 6·73 | 3·14 | 23·83 | — | 0·58 | 33·44 | 0·68 | — | 99·35 |
| III. | 29·68 | 64·94 | trace | — | — | 1·15 | 0 28 | — | — | 3·86 | 99·91 |

| | BaO. | MgO. | $K_2O$. | Total. |
|---|---|---|---|---|
| I. cont. | 1·45 | 1·08 | 12·85 | 99·69. |

L. J. S.

**[Babingtonite, Biotite, Almandine, and Gedrite from Massachusetts.]** By Benjamin K. Emerson (*Zeits. Kryst. Min.*, 1897, **28**, 502—504; from *Bull. U.S. Geol. Survey*, 1895, No. **126**, 1—180). —All the published information respecting the minerals found in Franklin, Hampshire, and Hampden counties, Massachusetts, is collected together in lexicon form, several new analyses, crystallographic and other observations, being also included. Babingtonite occurs as a black layer, sometimes showing crystal faces, coating fissures in the gneiss at Buckland; it gave analysis I, by E. A. Schneider, also a trace of boric acid. Biotite, from mica-schist at Goshen, gave II, by G. Steiger. Almandine crystals, from the schists at Goshen, enclose radially arranged bands of quartz grains; analysis III (Steiger). Gedrite forms a rock at Warwick; the brown crystals are optically negative and moderately pleochroic, and enclose rutile; analysis IV, (Schneider), also 0·05 $P_2O_5$.

| | $SiO_2$. | $TiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MnO. | CaO. | MgO. | $K_2O$. | $Na_2O$. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I. | 52·48 | trace | 1·91 | 23·24 | | 0·37 | 19·31 | 1·55 | — | — | 1·44 | 100·00 |
| II. | 36·96 | 0·91 | 21·15 | 2·80 | 15·54 | — | 0·23 | 7·87 | 7·47 | 1·00 | 2·93 | 96·86 |
| III. | 37·30 | 0·24 | 21·84 | 0·98 | 32·62 | 1·86 | 3·19 | 2·50 | — | — | — | 100·53 |
| IV. | 47·86 | 0·63 | 14·09 | 0·33 | 13·41 | 0·14 | 0·57 | 19·89 | 0·06 | 0·93 | 2·46 | 100·42 |

Several analyses of serpentine by Steiger are also given.

L. J. S.

**Garnet from Sardinia.** By Domenico Lovisato (*Jahrb. f. Min.*, 1897, ii, Ref., 32; from *Rend. R. Accad. Lincei*, 1896, **5**, i, 56—63).—In Sardinia, garnet occurs in Archæan rocks, in magnetite, in mineral veins, and in the younger volcanic rocks. At Caprera, it is abundant, with tourmaline, in a gneiss-like mica-schist; on the Punta rossa peninsula, these schists are cut by veins of a rose-red rock also containing much rose-red garnet in small crystals. Analysis by Fasolo gave:

| $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MnO. | CaO. | MgO. | Total. |
|---|---|---|---|---|---|---|---|
| 37·80 | 18·03 | 3·20 | 23·40 | 17·04 | 0·48 | 0·34 | 100·29. |

It is therefore spessartite. Sp. gr. 4·1016. L. J. S.

**Perlitic Pitchstone from New South Wales.** By William F. Smeeth (*Jahrb. f. Min.*, 1897, ii, Ref., 83—84; from *Journ. and Proc. Roy. Soc., N.S.W.*, 1895, **28**, (for 1894), 306—320).—Pitchstone from the Tweed River, N.S.W., gave on analysis,

| $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | CaO. | MgO. | $K_2O$. | $Na_2O$. | $H_2O$. | Total. | Sp. gr. |
|---|---|---|---|---|---|---|---|---|---|
| 75·51 | 14·30 | 1·01 | 1·81 | 0·24 | 2·89 | 1·21 | 2·84 | 99·81 | 2·47 |

Corresponding with

| Quartz. | Sanidine. | Albite. | Hypersthene. | Glass. | Water. |
|---|---|---|---|---|---|
| 5·11 | 14·94 | 2·07 | 1·90 | 73·14 | 2·84 = 100. |

These minerals occur as phenocrysts in the glassy base. The presence of hypersthene in so acid a rock is remarkable; it encloses magnetite, zircon, and apatite. The glass contains $K_2O$, 0·78; $Na_2O$, 1·14 per cent.

The perlitic structure admirably shown by this rock is described in detail, and the so-called perlitic cracks in quartz are discussed (compare *Geol. Mag.*, 1896, **3**, 15). L. J. S.

**Quartz-mica-diorite from Val Camonica.** By CARLO RIVA (*Jahrb. f. Min.*, 1897, ii, Ref., 65—66; from *Atti. Soc. Ital. Sci. nat.*, 1896, **36**, 139—159).—A quartz-mica-diorite near Rino, in the Val Camonica, consists of oligoclase, brown mica, quartz and sphene; there is a little orthoclase, but no hornblende. Analysis gave the results under I; under II is the analysis of a similar rock from Val Moja in the Adamello Mountains.

| | $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | CaO. | MgO. | $K_2O$. | $Na_2O$. | $H_2O$. | Total. |
|---|---|---|---|---|---|---|---|---|---|---|
| I. | 65·73 | 16·20 | 2·66 | 1·68 | 3·12 | 1·28 | 1·89 | 4·12 | 1·47 | 98·15 |
| II. | 66·75 | 15·90 | 3·73 | 1·84 | 3·11 | 1·23 | 1·98 | 3·38 | 1·22 | 99·14 |

The surrounding phyllites, when unaltered, consist mainly of quartz with chlorite and a little felspar; near the diorite, they contain the following secondary minerals: biotite, andalusite, staurolite, cordierite, muscovite, tourmaline, and garnet. L. J. S.

**Gabbros of Arolla.** By A. BRUN (*Jahrb. f. Min.*, 1897, i, Ref., 474—475; from *Arch. Sci. phys. nat.*, 1894, **32**, 102—109).—The gneiss of the district of Mt. Collon and the Arolla Glacier, in the Pennine Alps, is cut by dykes of gabbro. This contains anorthite, labradorite, diallage, olivine, hypersthene, and hornblende, together with secondary actinolite, mica, &c. The following analyses of the rocks are by A. Brunet; in III there is also a trace of fluorine.

| | $SiO_2$. | $Fe_2O_3$. | FeO. | $Al_2O_3$. | CaO. | MgO. | $K_2O$. | $Na_2O$. | FeS. | MnO. | $H_2O$ | Total. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I. | 48·40 | — | 4·28 | 17·53 | 11·11 | 16·51 | 1·8 | | 0·52 | — | 0·76 | 100·91 |
| II. | 47·45 | 2·80 | 3·60 | 19·25 | 14·00 | 8·61 | 2·20 | 1·0 | trace | trace | 1·65 | 100·56 |
| III. | 41·55 | 11·38 | 1·35 | 21·40 | 7·80 | 12·20 | 0·24 | 0·80 | 0·50 | ,, | 3·65 | 100·87 |
| IV. | 48·90 | 2·52 | 3·20 | 18·08 | 14·10 | 11·43 | 0·25 | 1·53 | trace | ,, | 0·88 | 100·89 |
| V. | 47·00 | 2·31 | 3·20 | 23·67 | 11·40 | 8·72 | 0·7 | 2·4 | — | ,, | 0·62 | 100·02 |

L. J. S.

**Dyke Rocks from Alnö.** By NAIMA SAHLBOM (*Jahrb. f. Min.*, 1897, ii, 97—101).—The following analyses are given of Dyke rocks from the nepheline-syenite district of the Island of Alnö, Sweden. I. Nephelinite from S. Berge, consisting of a ground-mass of nepheline, altered to natrolite, and ægirite needles, with phenocrysts of ægirite and ægirite-augite; from the analysis, the mineralogical composition is calculated as, ægirite and ægirite-augite 23·2, natrolite 63·1, nepheline 8·7 per cent. II, Monchiquite from S. Berge, consisting of a colourless ground-mass of nepheline (or analcite), with pyroxene needles and large, violet-grey augite prisms; calcite, sphene, apatite and pyrites are also present. III, Ijolite-porphyry from Ås, consisting of a fine-grained mass of nepheline, pyroxene, and melanite, with some

apatite and pyrites, and phenocrysts of melanite and pyroxene; the analysis corresponds with, melanite, 30·4; ægirite and ægirite-augite, 30·5; nepheline 35·0 per cent. IV, Alnöite from Norrwik (also 0·25 fluorine) consisting of a ground-mass of calcite with melilite and a little brown mica, also much magnetite and perofskite, and phenocrysts of apatite and olivine; this rock is nearer to the true melilite-basalts than to typical alnöite.

| | $SiO_2$. | $TiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MnO. | CaO. |
|---|---|---|---|---|---|---|---|
| I. | 49·07 | 0·64 | 19·46 | 2·30 | 3·50 | 0·38 | 3·82 |
| II. | 42·57 | 2·50 | 15·90 | 2·10 | 6·85 | 0·79 | 10·55 |
| III. | 42·02 | 2·36 | 12·05 | 7·93 | 5·06 | 0·96 | 17·01 |
| IV. | 29·25 | 2·54 | 8·80 | 3·92 | 5·42 | trace | 17·86 |

| | MgO. | $K_2O$. | $Na_2O$. | $H_2O$. | $CO_2$. | $P_2O_5$. | S. | Total. |
|---|---|---|---|---|---|---|---|---|
| I. | 0·60 | 4·39 | 9·25 | 5·99 | trace | trace | — | 99·40 |
| II. | 3·18 | 3·88 | 4·71 | 2·00 | 4·87 | ,, | trace | 99·90 |
| III. | 2·18 | 3·15 | 4·95 | 0·67 | — | 1·66 | 0·54 | 100·54 |
| IV. | 17·66 | 2·45 | 0·77 | 2·61 | 6·00 | 2·86 | trace | 100·29 |

L. J. S.

**Green Earth from Monte Baldo.** By C. Wilhelm von Gümbel (*Jahrb. f. Min.*, 1897, ii, Ref., 33—35; from *Sitz.-Ber. Akad. München*, 1896, **26**, 545—604).—Green earth occurring, mixed with hornstone, as veins in Tertiary basalt-tuff on Monte Baldo, in the Tyrol and quite near to the Italian frontier, gave analysis I—III, by A. Schwager. It is of a dark bluish-green colour; sp. gr. 2·850—2·920; hardness 1 and $3\frac{1}{2}$. By long digestion with hydrochloric or sulphuric acid, the fine powder is completely decomposed, with separation of pulverulent silica. In thin sections, it has a cloudy appearance with aggregate polarisation.

| | $SiO_2$. | $TiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | FeO. | MnO. | CaO. | MgO. | $K_2O$. |
|---|---|---|---|---|---|---|---|---|---|
| I. | 54·80 | 0·22 | 7·38 | 13·12 | 7·09 | 0·18 | 0·20 | 3·18 | 8·48 |
| II. | 55·80 | 0·24 | 3·20 | 16·85 | 3·88 | 0·12 | 0·16 | 5·32 | 9·04 |
| III. | 54·84 | 0·10 | 1·22 | 19·16 | 4·39 | 0·28 | 0·24 | 5·34 | 9·75 |
| IV. | 50·36 | 0·02 | 7·04 | 19·13 | 3·95 | 0·06 | 0·91 | 4·08 | 6·62 |

| | NaO. | $Li_2O$. | $P_2O_5$. | $H_2O$. | Organic matter | Total. |
|---|---|---|---|---|---|---|
| I. | 0·62 | — | 0·10 | 4·99 | trace | 100·36 |
| II. | 1·12 | — | 0·07 | 4·67 | ,, | 100·47 |
| III. | 0·82 | — | — | 3·77 | ,, | 99·91 |
| IV. | 1·58 | 0·01 | 0·26 | 6·32 | | 100·34 |

Glauconite in reniform masses from Monte Brione, on Lago di Garda, gave IV, by Schwager. It closely resembles the green earth in appearance; the colour is dark grey to black, and the streak dirty blue-green. Sp. gr. 2·955 and 2·952; hardness 3. The glauconite is more easily decomposed by hydrochloric acid than the green earth; 2 per cent. acid dissolves, in 8 hours, 58·08 per cent. of the former, and 23·86 of the latter, the soluble portion in both cases having the same composition as glauconite. Caustic potash partially dissolves both minerals.

From the behaviour with acid, it is concluded that the Monte Brione glauconite is a simple mineral, although the analysis does not lead to

a definite formula. The green earth may, however, be a mixture. These minerals, which have many characters in common, are placed in the mica group; and for the green earth of volcanic rocks the name celadonite (seladonit) is retained, whilst that of sedimentary rocks is called glauconite. Near the Tyrolese-Italian border, these green earths are worked commercially for paints. L. J. S.

**Water of the Adler Spring at Wiesbaden.** By C. Remigius Fresenius and Heinrich Fresenius (*Jahrb. nassau. Ver. Naturk.*, 1897, **50**, 3—21).—The water of the Adler spring at Wiesbaden is slightly yellowish, and on standing gives an ochreous deposit; it has a temperature of 64·4°. Sp. gr. 1·00626 at 19°. In 1000 parts are: $Na_2O$, 3·626856; $K_2O$, 0·108983; $Li_2O$, 0·009217; $NH_4$, 0·004778; CaO, 0·499457; BaO, 0·000287; SrO, 0·013545; MgO, 0·078575; FeO, 0·004025; MnO, 0·000758; Cl, 4·666173; Br, 0·003818; I, 0·000032; $SO_3$, 0·056197; $P_2O_5$, 0·000030; $As_2O_5$, 0·000119; $B_2O_3$, 0·000986; $SiO_2$, 0·062262; total $CO_2$, 0·593732. Total solids 8·342868; free $CO_2$, 0·142038. Rubidium, cæsium, copper, titanic acid, nitric acid, hydrogen sulphide and organic matter are also present in minute traces. The composition of this water is like that of all the other warm salt springs of Wiesbaden (this vol., ii, 109); it is compared with that of the Kochbrunnen. L. J. S.

**Mineral Waters in Canton Graubünden.** By Gustav Nussberger (*Jahresber. Naturf. Ges. Graubünden's*, 1896, **39**, 67—76).—Mineral waters, rich in calcium sulphate, from springs in the Canton Graubünden (Grisons), Switzerland, gave the following results on analysis, in parts per 10,000. I, Springs at Juf. II, Sassal spring; temperature, 8·1°; sp. gr. 1·0011; also MnO, 0·0100. III, Peiden springs in the Lugnetz-thal; temperature 12·2°; sp. gr. 1·00365. IV, Spring in the Val d'Urezza; temperature 7·3°; sp. gr. 1·0011; also trace of organic matter.

| | CaO. | MgO. | FeO. | $K_2O$. | $Na_2O$. | $SO_3$ | $SiO_2$. | Cl. | $CO_2$. |
|---|---|---|---|---|---|---|---|---|---|
| I. | 6·458 | 0·483 | — | — | — | 9·533 | 0·256 | trace | — |
| II. | 2·5175 | 0·4554 | 0·0045 | 0·0594 | 1·3302 | 0·3390 | 0·0265 | 0·0161 | 22·8590 |
| III. | 7·9970 | 1·2450 | 0·1206 | 0·3779 | 5·2110 | 9·2858 | 0·2450 | 1·3430 | 23·3720 |
| IV. | 4·6949 | 0·1559 | 0·0137 | trace | 0·0231 | 6·4873 | 0·0770 | 0·0201 | 1·0695 |

Analysis is also given of water from a spring at Rhäzüns.

L. J. S.

## Physiological Chemistry.

**Amount of Hæmoglobin in the Blood at High Altitudes.** By Piero Giacosa (*Zeit. physiol. Chem.*, 1897, **23**, 326—342).—The method of estimating hæmoglobin adopted was a colorimetric one, the instrument used being a new one, which is fully described and figured.

The results show that a long stay at great altitudes causes an appreciable increase in the blood pigment. A shorter stay so that acclimatisation does not occur, or a longer stay at lower elevations,

causes little or no change; the variations are small, and differ in different species of animals and in different animals of the same species; in man there is a tendency to increase. W. D. H.

**Absorption of Iron and Synthesis of Hæmoglobin.** By JUSTUS GAULE (*Zeit. Biol.*, 1897, **35**, 377—393).—The presence of iron in the chyle after the administration of inorganic salts of iron is regarded as evidence that the iron is absorbed. In rabbits, this is followed by a marked and rapid rise in the number of blood corpuscles, and of the percentage of hæmoglobin in the blood. The spleen increases in weight, and microchemical examination of this and other organs shows that the synthesis of new blood pigment probably occurs principally in the spleen, and, to a less extent, in the liver and bone marrow. W. D. H.

**Reducing Substances in the Blood.** By VALDEMAR HENRIQUES (*Zeit. physiol. Chem.*, 1897, **23**, 244—257).—The experiments performed on the blood of dogs and rabbits show that, in addition to the glucose preformed in it, the blood will yield an extra amount after boiling with sulphuric acid; this comes from jecorin; in fact, the sugar which originates from jecorin is from three to five times as abundant as that which is already preformed. W. D. H.

**Animal Life without Bacteria in the Alimentary Canal.** By GEORGE H. F. NUTTALL, and HANS THIERFELDER (*Zeit. physiol. Chem.*, 1897, **23**, 231—235).—Previous portions of this research have shown that, in mammals, healthy life is possible without the presence of becteria in the alimentary tract. The present observations made on hen's eggs were undertaken with the hope of finding no bacteria in the interior of the egg shell in fresh eggs, and during development. This hope was not fully realised, as the greater number of eggs are infected with bacterial growths, which are derived from the oviduct before and during the formation of the shell.

W. D. H.

**Influence of Muscular Exercise, Sweating, and Massage on Metabolism.** By JAMES C. DUNLOP, DIARMID NOËL PATON, RALPH STOCKMAN, and IVISON MACADAM (*J. Physiol.*, 1897, **22**, 68—91).—The experiments performed on various human subjects on fixed diet, show that after excessive exercise there is in the urine an increase of total nitrogen (which is chiefly accounted for by increase of urea) of preformed ammonia, of creatinine, and of sulphates (proportionate to the nitrogen). With concomitant sweating, there is diminution of the water, chlorides, and sodium. When the subject is in poor condition, there is a rise of uric acid, nitrogenous extractives, and phosphoric acid.

The general conclusion drawn is that increase of work leads to increased katabolism of the proteid of muscle; this is supported by the fact that uric acid, extractives, and phosphoric acid, are not increased, muscle being poor in nucleo-proteids. The importance of such a conclusion on the training of athletes is pointed out. Experiments on massage gave negative results. W. D. H.

**Acetone as a Metabolic Product.** By H. CHR. GEELMUYDEN (*Zeit. physiol. Chem.*, 1897, **23**, 431—475).—Acetonuria occurs when insufficient carbohydrate food is given. 100—200 grams *per diem* are necessary for an adult man. A purely proteid diet produces slight acetonuria. During hunger, or a mixed proteid and fat diet, or a purely fat diet, the acetonuria is considerable. The organism possesses the power of destroying acetone in some degree; but this is not sufficient to hinder acetonuria if the amount of acetone in the circulating fluids of the body is more than the normal traces. (Compare Hirschfeld, this vol., ii, 422.) W. D. H.

**Hepatic Glycogenesis.** By DIARMID NOËL PATON (*J. Physiol.*, 1897, **22**, 121—136). — This is a further contribution to the long-sustained controversy between the author and Pavy. Some of the experiments previously published are withdrawn, but the general conclusion is still maintained that the conversion of glycogen into glucose is the result of katabolic changes in the liver substance, and not of the action of an amylolytic zymin (enzyme). W. D. H.

**The Mineral Constituents of Human Organs.** By WACLAW VON MORACZEWSKI (*Zeit. physiol. Chem.*, 1897, **23**, 483—496).—Previous work has shown that in anæmia the urine is rich in phosphorus and poor in chlorine; in the blood, the converse is true. In pneumonia, both the urine and blood are poor in chlorine and rich in phosphorus. There is, therefore, in some diseases, a retention of chlorine in the body, but this can only be proved by an estimation of the mineral salts of the organs. The present paper gives numerous analyses relating to this point; they do not, however, bear out fully the expectations of the author; they show increase of chlorine in cases of anæmia, and decrease in phosphorus and calcium. The organs are also more watery. W. D. H.

**The Mineral Matters in Birds' Bones.** By FRANZ DÜRING (*Zeit. physiol. Chem.*, 1897, **23**, 321—325).—Several observers have stated that the amount of mineral matter in the bones of birds is greater than in those of mammals; Weiske, on the other hand, affirms that the percentage is lower. In the present communication, which gives numerous analyses, it is shown that the whole skeleton of various birds contains less (59—63 per cent.) mineral matter than the bones of mammals, in which the average percentage is 66. These percentages are reckoned for bone free from water and fat. If individual bones are taken, however, the long bones are found to be richer in mineral salts (up to 69 per cent.) than the flat bones, where the highest percentage found was 61. W. D. H.

**The Sulphuric Acid in Bone-ash.** By CARL TH. MÖRNER (*Zeit. physiol. Chem.*, 1897, **23**, 311—320).—Weiske has stated that the natural substance of bone contains no sulphuric acid; nevertheless, its ash contains that compound, and this is derived from the sulphur of the organic substratum of osseous tissue called collagen. In the present research, it is shown that if a gas burner is used in the process of incineration, a not inconsiderable quantity of sulphuric acid is derived from the gas. This is, however, not the only source of the

compound, for a small quantity is found when a spirit lamp is employed. This varies in quantity in different bones, and originates from chondroitin-sulphuric acid. W. D. H.

**Distinction between Organic and Inorganic Compounds of Iron.** By A. B. Macallum (*J. Physiol.*, 1897, **22**, 92—98).—In microscopic preparations of tissues, the ammonium sulphide and prussian blue reactions are not always satisfactory in deciding the question whether granules are composed of "organic" or "inorganic" compounds of iron. The best reagent is found to be a 0·5 per cent. aqueous solution of pure hæmatoxylin. This does not affect organic iron compounds, but stains inorganic compounds bluish-black. Ferratin, carniferrin, and peptonates and albuminates of iron give the blue reaction, and are therefore classified as "inorganic." "Organic" compounds may be converted into "inorganic" by the action of acidified alcohol. This, however, is not the case with hæmoglohin and hæmatin. W. D. H.

**Iodine in the Hairs.** By W. Howald (*Zeit. physiol. Chem.*, 1897, **23**, 209—225).—There is no iodine or bromine in normal human hairs; but very soon after the usual medicinal doses of iodide or bromide of potassium, iodine or bromine respectively may be detected in the hairs. This disappears when the drug is discontinued and the hair has been repeatedly cut. The halogen is probably in an organic combination, and is introduced in the new hair which grows during the use of the drug. W. D. H.

**The Amount of Iodine in Thyroid Glands.** By Ad. Oswald (*Zeit. physiol. Chem.*, 1897, **23**, 265—310).—A very large number of determinations of the amount of iodine in thyroids are given; the greater number of these were human, removed after death from various diseases in different Swiss Cantons. It was found that the amount of iodine in the gland was not inversely proportional to the prevalence of cretinism; in fact, thyroids in cases of cretinism in which the degenerative change had not gone so far as to replace the glandular with connective tissue, often contained more iodine than the healthy organ. The quantity of iodine in the thyroids of both men and animals is in direct proportion to the amount of colloid material in the acini. W. D. H.

**Presence of Iodine in the Parathyroid Glandules.** By Eugène Gley (*Compt. rend.*, 1897, **125**, 312—315).—The parathyroid glandules of rabbits were found to contain from 2·5 to 3 times as much iodine as the thyroid glands of the same animals. In the case of dogs, the absolute quantity of iodine in the parathyroid glandules is lower than that in the thyroid glands, but the percentage amount is much higher. It is clear that the glandules must be regarded as forming an important part of the thyroidien system. The exact relation between the gland and the glandules is under investigation. C. H. B.

**Chemistry of Spermatozoa.** By Albert Mathews (*Zeit. physiol. Chem.*, 1897, **23**, 399—411).—The spermatozoa of the sea urchin *Arbacia* contain no protamine, but instead a histon-like substance to

which the name *arbacin* is given. The chromatin of these spermatozoa is partly, if not exclusively, a union of nucleic acid with arbacin. The nucleic acid has the same percentage of nitrogen and phosphorus as that obtained from the salmon.

The chromatin of herrings' spermatozoa is a compound of protamine and nucleic acid ($C_{30}H_{57}N_{17}O_6,C_{40}H_{54}P_4N_{14}O_{27}$).

The spermatozoa of the bull and boar contain either protamine or a histon extractable by the use of sulphuric acid. W. D. H.

**Physiological Action of Chlorhydrins.** By C. R. Marshall and H. Ll. Heath (*J. Physiol.*, 1897, **22**, 38—60).—The introduction of chlorine atoms into a fatty compound increases its narcotic power. The toxic power is also increased if the solubility of the compound formed is not diminished. Thus dichlorhydrin is more of an irritant than trichlorhydrin, because it is more soluble; the irritant action is seen in the alimentary canal and kidney. The action on muscular tissue increases with each increment of chlorine; as this action is exhibited also on involuntary muscle, the circulation is enfeebled.

W. D. H.

**Behaviour of Phenylglycine and Phenylglycinorthocarboxylic Acid in the Animal Body.** By Jörgen E. Thesen (*J. Physiol. Chem.*, 1897, **23**, 23—29).—See this vol., i, 618.

**Physiological Effects of Extracts of Suprarenal Capsules.** By Swale Vincent (*J. Physiol.*, 1897, **22**, 111—120).—Large doses of suprarenal extract injected subcutaneously produce muscular weakness and finally paralysis, hæmorrhage in various parts, irregularity in the breathing, and fall of temperature. The paralysis is central.

The cortex of the capsules contains no toxic substance. The toxic material of the medulla is rapidly eliminated, hence the largeness of the dose required. A partial immunity can be set up by giving doses not sufficient to kill. W. D. H.

**Antagonistic Action of Digitalis and Nitrites.** By C. R. Marshall (*J. Physiol.*, 1897, **22**, 1—37).—Digitalis counteracts the effect of members of the nitrite group on blood-vessels, but the influence of the latter in antagonising digitalis is much more powerful.

W. D. H.

**Phosphorus in Human and Cow's Milk.** By Julius Stoklasa (*Zeit. physiol. Chem.*, 1897, **23**, 343—346).—Siegfried states that the phosphorus of human milk is almost exclusively in combination in casein and nucleon (phosphorcarnic acid).

This leaves lecithin altogether out of account. The present analyses show that a litre of human milk contains 0·44 gram $P_2O_5$, and of cow's milk 1·81 grams; of this 0·153 gram (or 35 per cent.) and 0·091 (or 5 per cent.) respectively are obtained from the lecithin present. This, and other facts render a comparison between milk and embryo-plants interesting. It is stated that phosphorcarnic acid is widely distributed in vegetable organisms, and comes into prominence especially during germination and blossoming. W. D. H.

**Asses Milk.** By Arthur Schlossmann (*Zeit. physiol. Chem.*, 1897, **23**, 258—264).—Asses milk is white, with a bluish opalescence; it is faintly sweet, like diluted cow's milk; the fat globules as seen under the microscope are scanty in comparison with those in cow's and human milk. One c.c. has an alkalinity equal to 0·404 c.c. of decinormal sulphuric acid, and an acidity equal to 0·06 c.c. of decinormal sodium hydroxide. Its sp. gr. varies from 1·031 to 1·036; it contains,

| | | |
|---|---|---|
| Dry residue | 11·15 | per cent. |
| Ash | 0·40 | ,, |
| Fat | 0·36 | ,, |
| Sugar | 4·94 | ,, |
| Phosphorcarnic acid | 0·12 | ,, |
| Total nitrogen | 0·24 | ,, |

Three-quarters of the proteids consist of caseinogen, the remaining quarter being lactalbumin; these account for 86 per cent. of the nitrogen. The small quantity of fat shows how greatly asses milk differs from human milk, with which it is often compared. W. D. H.

**Behaviour of Animal and Vegetable Foods in the Alimentary Canal. Introduction.** By Wilhelm Prausnitz (*Zeit. Biol.*, 1897, **35**, 287—290). **Vegetable Matter in Human Fæces.** By Joseph Moeller (*ibid.*, 291—315). **Flesh in Human Fæces.** By Fritz Kermauner (*ibid.*, 316—334). **Chemical Composition of the Fæces with Different Diets.** By Wilhelm Prausnitz (*ibid.*, 335—354). **Bacteria of Human Fæces.** By Hans Hammerl (*ibid.*, 355—376).—This forms a series of investigations, microscopical, chemical, and bacteriological, on the composition of human fæces. From the nutritional standpoint, such work is essential for the estimation of the value of a diet. Each paper is prefaced by a summary of previous work on the same subject.

Microscopical examination of the fæces after vegetable diet shows a considerable amount of vegetable *débris*, principally of the nature of membranes, and cellulose. Starch grains, after the administration of potatoes and cereals, are hardly ever found.

After an abundant meat diet, muscular fibres in very small quantities form a constant constituent of the fæces, and the amount was roughly estimated by a microscopical comparison of the fæces with some of the same material intimately mixed with a known quantity of finely divided flesh.

In the chemical investigation of the excrements after diets of various kinds, particular attention is given in the analyses to total solids, nitrogen, fat, and ash. By the use of a diet the constituents of which are almost completely absorbed, like rice, meat, baked finely divided wheat meal, there is in the fæces 8—9 nitrogen, 12—18 ether extract, and 11—15 ash per cent.

In comparison with this "normal," the nitrogen usually falls when the diet is less well absorbed; although in a few cases, when nutriment of high nitrogenous value is given, it rises.

The secretions from the intestines always form a very considerable factor in the composition of the fæces, and the quantity of fæces, therefore, depends on the nature rather than on the amount of the food given.

In some apparent exceptions to these rules, a relatively low percentage of nitrogen is produced by a relative increase of ash and fat.

No characteristic difference between the use of animal and vegetable diet is observable. W. D. H.

**Stercorin.** By AUSTIN FLINT (*Zeit. physiol. Chem.*, 1897, **23**, 363—367).—Bondzynski and Humnicki have given the name koprosterol to a constituent of human fæces which is derived from cholesterol (Abstr., 1896, ii, 320). It is shown that this is no new material, but is identical with the substance named stercorin by the author, and described by him many years ago. W. D. H.

**The Nitrogenous Constituents of the Urine.** By WILLIAM CAMERER (*Zeit. Biol.*, 1897, **35**, 206—251).—A large number of observations on human urine, in which the influence of diet, age, work, gout, &c., on the amount of total nitrogen, urea nitrogen, uric acid nitrogen, and nitrogen of alloxuric bases are given. In connection with the estimation of the last-named substances, the rreat discrepancies between the results obtained by previous observers a e pointed out. W. D. H.

**Uric Acid Formation in Man.** By WILLIAM J. SMITH JEROME (*J. Physiol.*, 1897, **22**, 146—158).—The research relates to the influence of diet on the formation of uric acid. If nuclein is introduced in the food, the alloxan group appears in the urine, partly as uric acid; and the variations in the amount of the latter are believed to be chiefly due to the amount of nuclein in the food. The uric acid passed during fasting is, doubtless, attributable to katabolism of nuclein-holding cells in the body. W. D. H.

**Urinary Sediments and Gout.** By A. RITTER (Carlsbad) (*Zeit. Biol.*, 1897, **35**, 155—182).—The paper is principally a discussion of the possible ways in which, by an interaction of the phosphates and urates in the urine, free uric acid may be deposited. The views of Garrod in relation to the cause of gout are subjected to criticism. In the tables of analyses given, it is shown that, in many cases in which there is a deposit of uric acid crystals, there is no increase in the absolute amount of uric acid; indeed, in cases where the acid is deposited as urates, the uric acid is more abundant. W. D. H.

**Constituents of Urine Precipitated by Phenylhydrazine.** By MAX JAFFÉ (*Zeit. physiol. Chem.*, 1897, **22**, 532—537).—*Phenylsemicarbazide from the urine of dogs.*—When the urine of dogs, which have been fed on meat, is treated with phenylhydrazine and acetic acid, a large amount of a yellow, crystalline precipitate is obtained, which proved to be identical with phenylsemicarbazide, first obtained by E. Fischer (*Annalen*, **190**, 130) from phenylhydrazine hydrochloride and potassium cyanate.

The author was unable to isolate this substance from the urine of dogs fed on bread or milk, or from human urine after mixed diet.

Phenylsemicarbazide is produced almost quantitatively on warming a solution of carbamide (10, 5, 3, or 2 per cent.) with phenylhydrazine and acetic acid.

The presence of ethylcarbamide in the urine of a dog could not be

proved, although the isolation of its phenylhydrazine compound was attempted. A. W. C.

**Kynurenic Acid.** By ACHILLE CAPALDI (*Zeit. physiol. Chem.*, 1897, **23**, 87—91).—Haagen has observed that the amount of kynurenic acid in the urine of a dog is lessened when the animal is fed with sterilised instead of raw meat. The author points out that it is impossible to attribute this fact to the decrease of putrefactive matter in the intestine, as this cannot have the least influence on the intensity of the bacteriological decomposition. Nevertheless, experiments were made which prove conclusively that the bacteria of the intestines produce no kynurenic acid nor any substance which, after absorption by the tissues, is changed into this acid. Moreover, kynurenic acid is not formed by the action of the secretion of the pancreas of a dog on proteids, nor is it formed in the intestines themselves. A. W. C.

**Kynurenic Acid.** By P. SOLOMIN (*Zeit. physiol. Chem.*, 1897, **23**, 497—504).—In the dog, the daily excretion of kynurenic acid and of uric acid vary a great deal; but there is no constant relationship between the two. If isatin is given, it is not excreted as kynurenic acid; tyrosine also is not a parent substance of this acid. If kynurenic acid is given subcutaneously, it is in part excreted in the urine as such; but in men and rabbits the percentage excreted is much less, as they have apparently more power to destroy it. W. D. H.

**Alcaptonic Acids.** By KARL H. HUPPERT (*Zeit. physiol. Chem.*, 1897, **23**, 412—416).—In recent cases of alcaptonuria, the acid found has been homogentisic acid; but to this a case recorded by Kirk forms an exception, he having described the acid as uroleucic. From some of the raw material from this case, attempts were made in the present research to obtain homogentisic acid, and it was found; Kirk's case is therefore no exception. Uroleucic acid was, however, found as well, although in smaller quantities. The properties of the two acids are very similar; the former contains two hydroxyl groups, the latter three, two united to the benzene nucleus, the third in a side chain.

Methylated uroleucic acid gives the same oxidation product as methylated homogentisic acid; uroleucic acid is probably dihydroxyphenyl-lactic acid, $C_6H_3(OH)_2 \cdot CH_2 \cdot CH(OH) \cdot COOH$, and this coincides with the view held as to the origin of homogentisic acid from tyrosine.

W. D. H.

**Chronic Oxalic Acid Poisoning.** By W. CASPARI (*Bied. Centr.*, 1897, **26**, 529—533; from *Inaug. Diss. Berlin*). **Feeding Experiments with Turnip Leaves.** By NATHAN ZUNTZ (*ibid.*, 533—534; from *D. Landwirt*, 1896, No. 74).—Experiments in which rabbits were fed with turnip leaves and meal, with meal, bran, and oxalic acid, with excess of calcium carbonate and hydrogen sodium carbonate, showed that oxalic acid in the form of sodium salt is the most injurious, owing, partly, to loss of lime and consequent weakening of the bones. The calcium salt was least injurious, whilst the turnip leaves, which contain both sodium and calcium oxalate, were less injurious than sodium oxalate, and more so than calcium oxalate. Another rabbit, which

received nearly 200 grams of oxalic acid as calcium salt, was less injured than one which had only 11 grams as sodium salt.

Further experiments, made with dogs, showed that the consumption of oxalic acid gave rise to increased amounts of lime in the fæces and urine. When given for a short time, in small amount, and in a not too soluble form, oxalic acid acts beneficially by increasing the appetite. In larger quantity, it is poisonous, injuring the bones and kidneys, and perhaps the heart.

Zuntz refers to von Nathusius's experiments, in which sheep which received food containing oxalic acid for 6 months were not injured; this was shown to be due to the destruction of the oxalic acid in the sheep's rumen. The contents of the rumen of a sheep which had been fed with oxalic acid destroyed a measured quantity of sodium oxalate in 24 hours [the amount is not stated]. Sheep which have not been fed with oxalic acid have not this power, or at least not to the same extent.

With pigs, the same results were obtained as with rabbits and dogs; the bones became so weak that the animals could scarcely stand, and the solid excrement contained large amounts of lime. N. H. J. M.

**Clinical Significance of Lactic Acid.** By J. H. de Jong (*Chem. Centr.*, 1896, ii, 806—807. See this vol., ii, 607).

---

## Chemistry of Vegetable Physiology and Agriculture.

---

**Behaviour of Yeast at a High Temperature.** By T. Nakamura (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, 3, 227—230).—A pure cultivation of yeast was grown in a solution of cane-sugar (10 per cent.) and meat extract (0·5 per cent.), the supernatant liquid poured off, and the sediment washed with sterilised distilled water. It was then suspended in sterilised water, and 5 c.c. of the mixture placed in a test tube closed with a cotton plug, and exposed for several minutes to a constant temperature. The yeast was not destroyed by exposure for 1½ hour at 46°, or for 2 hours at 48°, but was completely destroyed by a temperature of 52° in 20 minutes. Exposure to a temperature of 50° destroyed the yeast in 30 minutes, but not in 29 minutes.

The results of other observers, who state that yeast is destroyed at 40°, is ascribed to the fact that, after being heated, yeast never produced fermentation in Pasteur's solution as quickly as the control sample, the retardation sometimes amounting to several days.

As regards the effect of different compounds in enabling yeast to resist the action of heat, experiments were made in which the yeast was suspended in various solutions and heated at 50° for 30 minutes, and the effect, after addition of sterilised Pasteur's solution, observed. With distilled water, cane-sugar solution (10 per cent.), sodium sulphate (1 to 10 per cent.), and disodium phosphate (1 to 10 per cent.), there was no fermentation; with sodium chloride (1 to 10 per cent.), there was only fermentation after heating in the 3 per cent. solution; with sodium nitrite (1 to 10 per cent.), there was only fermentation in

the case of the 2 per cent. solution; with meat extract (0·5 per cent.), there was normal fermentation. Only the last three solutions had, therefore, the effect of increasing the resistance towards heat.

OSCAR LOEW (*ibid.*, 230—232) calls attention to the soluble proteid recently obtained by Buchner by expressing yeast (this vol., ii, 154). He considers it probable that the proteid is intimately connected with the living protoplasm, and that the greater part of it remains within the cells, where most of the sugar would be fermented. It will be of interest to examine the effect of diamide, hydroxylamine, hydrogen cyanide, &c., on the zymase, on the one hand, and of cyanogen, formaldehyde, &c., on the other (compare Loew, *Pflüg. Arch.*, **27**, 208, and Abstr., 1888, 607). N. H. J. M.

**Two New Kinds of Red Yeast.** By K. YABE (*Bull. Coll. Agr. Imp. Univ. Tokyo*, 1897, **3**, 233—236).—The two new species of yeast were obtained from the soil of rice fields and from rice straw. They both resemble *Saccharomyces rosaceous* in not forming ascospores, but differ from it in other respects.

*Saccharomyces Japonicus.*—The cells are elliptic, and approach a more globular form when well nourished with meat extract. Size = $6 \times 3\ \mu$ (in Pasteur's solution) and $9{\cdot}2 \times 5{\cdot}1\ \mu$ to $10{\cdot}3 \times 6{\cdot}1\ \mu$ (in meat extract). It grows well on potato, and acquires a brilliant red tint. It is unable to produce alcohol from glucose or cane-sugar, and its development is retarded in presence of 3 per cent. of alcohol, and altogether stopped by 7 per cent. A temperature of 45° for 15 minutes destroys the cells.

*S. Keiskeana.*—Globular cells $5{\cdot}1\ \mu$ to $9\ \mu$ in diameter. It forms a faintly pink deposit in Pasteur's solution, but the colour is brighter on potato, probably owing to the effect of free oxygen. A moderate growth is obtained in starch-culture in sugar-gelatin, but the cells remain colourless, whilst those on the surface gradually acquire a pink colour. The cells are killed by heating for 15 minutes at 50°, but not at 46°. Development is retarded by 5 per cent. and stopped by 7 per cent. alcohol. N. H. J. M.

**Production of Carbon Bisulphide by Schizophyllum lobatum.** By F. A. WENT (*Chem. Centr.*, 1896, ii, 939; from *Ber. deut. bot. Ges.*, 1896, 158—163, and *Centr. Bakt. Par.*, **2**, ii, 528).—A cultivation of *Schizophyllum lobatum* in sugar-peptone yielded carbon bisulphide when distilled; in hydrogen, the fungus produces no carbon bisulphide, or only traces. When cultivated, with peptone as the source of nitrogen, an alcohol (probably ethylic alcohol) is formed, and in absence of air, there is active fermentation, the amount of carbonic anhydride produced being considerably greater than with access of air.

The fungus occurs in Java on old, fallen branches of *Pedocarpus*, and on dead bamboo stems, &c. N. H. J. M.

**Decomposition of Fibrin by Streptococci.** By OSKAR EMMERLING (*Ber.*, 1897, **30**, 1863—1868. Compare this vol., ii, 113).—The experiments were made with pure cultures of *Streptococcus longus Petruschky*, and with fibrin from the blood of freshly-killed pigs. Four kilograms of fibrin were added to 3 litres of water, and the

whole sterilised by heating at 100° for 2 hours a day during 4 days; the mixture was then inoculated and kept in an incubator at 40° for 3 weeks, when the products of decomposition were investigated. For this purpose, the liquid, after filtration through a Pukall's filter, was distilled at 40° under diminished pressure; the solution, which was faintly alkaline at the beginning, became acid, whilst the distillate was strongly alkaline, and from it the author obtained ammonia, methylamine, and trimethylamine. The following substances were obtained from the residue after evaporation: tyrosine, leucine, acids of the fatty series from acetic to caproic (with the exception of valeric acid), succinic acid, trimethylamine, and a basic substance having the composition of a collidine, although apparently differing from any of those already known. Peptonic substances were also obtained, and their physiological action tested. No poisonous substances could be isolated by the method described. J. J. S.

**Decomposition of Elastin by Anærobic Micro-organisms.** By LUIGI ZOJA (*Zeit. physiol. Chem.*, 1897, **23**, 236—243).—Elastin was prepared from the *ligamentum nuchæ* of the ox, by a method which differs only in small details from that adopted by Horbaczewski and by Chittenden and Hart. The putrefaction was carried out in a Hoppe-Seyler flask, air being excluded; the gases obtained consisted of carbonic anhydride 90·46, hydrogen 4·74, methane 2·37, and nitrogen 2·43 per cent. Two days after the evolution of gas ceased, the experiment was stopped, and much material was still undissolved; the sulphur is eliminated as mercaptan and not as hydrogen sulphide. In the distillate, valeric and butyric acids were found, whilst the residue gave phenylpropionic acid, aromatic hydroxy-acids, and ammonia.

W. D. H.

**Chemical and Bacteriological Investigation of the Fermentation of Fresh Grass.** By OSKAR EMMERLING (*Ber.*, 1897, **30**, 1869—1870).—Freshly cut grass was pressed into a large earthenware vessel, closed by a lid into which fitted a thermometer and delivery tube. The composition of the grass was: woody tissue 26·4, ether extract 1·86, proteids 11·8, ash 7·62, and non-nitrogenous extract 52·32 per cent., calculated on the dry substance. At the end of 24 hours, the temperature had risen to 26°, at which point it remained stationary for some time, and then gradually sank to the temperature of the room. For 4 weeks, a slow but continuous evolution of gas, consisting of 64 per cent. carbonic anhydride and 36 per cent. nitrogen, took place. At the end of this period, the grass had the composition: woody tissue 31·36, ether extract 3·24, proteids 9·13, ash 8·14, and non-nitrogenous extract 48·13 per cent. The increase in the ether extract was largely due to the presence of organic acids, formed mainly at the expense of the non-nitrogenous extract, that is, carbohydrates. The hay thus formed possessed a somewhat pleasant ethereal odour, and at the same time a pungent odour which was found to be due to quinone.

Among the organisms isolated were small quantities of moulds, chiefly species of *mucor*; and, besides hay bacteria, granulobacter and coccus species, *Bacillus mycoides* was found. It has been shown that

the latter organism is capable of fermenting glucose, yielding inactive lactic acid; and that it is also capable of hydrolysing cane-sugar, maltose, and glycogen. No other lactic acid bacterium could be isolated.

J. J. S.

**An Important Function of Leaves.** By U. Suzuki (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, 3, 241—252).—As it is known that, during the night, a considerable amount of carbohydrates in the leaves migrate to other parts of the plant, it seemed probable that a corresponding amount of proteids are also transported from the leaves, since the decrease of the protecting carbohydrates must involve an attack on the reserve of proteids formed during the day. One experiment has already been made in this direction by Sapoznikow (Abstr., 1896, ii, 537).

The following results were obtained with the leaves of a number of plants which were cut at 6 a.m. and 6 p.m. respectively. The plants selected for experiment were: (1) *Wistaria brachybotrys*; (2) *Phaseolus mungo*; (3) *Phaseolus vulg.*; (4) *Pueralia Thumbergiana*; (5 and 6) *Solanum tuberosum*; (7) *Batatas edulis*; (8) *Polygonum fagopyrum* and (9) *Helianthus annuus*. The numbers show the absolute amounts (in grams) in 100 leaves.

| | Evening. | | | | | Morning. | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | N. | N. as proteids. | N. as asparagine | N. as amides.* | Starch. | N. | N. as proteids. | N. as asparagine. | N. as amides.* | Starch. |
| 1. | 0·1725 | 0·1457 | 0·0050 | 0·218 | 0·4848 | 0·1490 | 0·1215 | 0·0058 | 0·0217 | 0·2611 |
| 2. | 0·8160 | 0·6610 | 0·0300 | 0·1250 | 2·0520 | 0·7270 | 0·5955 | 0·0170 | 0·1145 | 1·4560 |
| 3. | 0·8660 | 0·7021 | 0·0510 | 0·1129 | 5·8970 | 0·8290 | 0·6260 | 0·0490 | 0·1540 | 3·9350 |
| 4. | 1·887 | 1·516 | 0·112 | 0·126 | — | 1·797 | 1·559 | 0·112 | 0·260 | — |
| 5. | 0·3350 | 0·2517 | 0·0230 | 0·0603 | 0·9600 | 0·3067 | 0·2390 | 0·0163 | 0·0514 | 0·4134 |
| 6. | 0·1944 | 0·1552 | 0·0130 | 0·0260 | — | 0·1791 | 0·1414 | 0·0235 | 0·0142 | — |
| 7. | 1·566 | 1·238 | 0·152 | 0·176 | — | 1·504 | 1·186 | 0·210 | 0·108 | — |
| 8. | 0·1798 | 0·155 | 0·0091 | 0·0156 | — | 0·1649 | 0·1435 | 0·0048 | 0·0166 | — |
| 9. | 3·976 | 2·990 | 0·226 | 0·760 | 7·066 | 3·590 | 3·000 | 0·344 | 0·246 | 5·535 |

* Excluding asparagine.

The results show in most cases a decrease of total and proteid nitrogen, more or less corresponding with the loss of starch. The exceptions in the case of *Helianthus* (9) and *Pueralia* (4) are explained by the fact that the evening leaves were not dried immediately and had therefore remained alive during the night, so that a decomposition of proteids might have occurred with accumulation of amides. This was shown by another experiment to actually take place.

It is therefore established that leaves possess the important function of facilitating the formation of proteids in all parts of the plant by assimilating nitrates, yielding thereby amido-compounds. A great advantage is thus gained for the stems, roots, and fruit, in which the conditions for the assimilation of nitrates are less favourable than in the leaves.

The author thinks that Kosutany's results (this vol., ii, 115) cannot be considered conclusive as regards the functions of leaves under discussion. Kosutany collected leaves at 4 p.m. and at 3 a.m. and the results would therefore show smaller differences than in the present case.

N. H. J. M.

**Production of Sugars in Beetroot.** By FRIEDRICH STROHMER (*Chem. Centr.*, 1896, ii, 847—848; from *Oestr.-ung. Zeit. Zucker.-Ind. u. Landw.*, **25**, 589—600).—The opinion expressed 30 years ago by H. Schacht, that the quality of beetroots depends on the number of developed leaves and the length of life of the plant, is now shown to be free from objections. Sugar is produced in the leaves either directly as reducing sugar, or from starch or other carbohydrate, and migrates through the leaf stems to the root. The production of sugar depends on the amount of light, and the form and position of the leaves are of importance. When the sunlight passed through white or yellow glass, leaf production was vigorous, but with blue or red glass, feeble; and the weight of roots under the influence of yellow light was nearly twice as great as when blue and red light were employed. The percentage of sugar under the different conditions was 7·4—8·1 with yellow, 6·4—7·4 with red, and 8·0—8·4 with blue light. For producing total organic substance in beetroot, rays of medium wave-length are the most favourable, but for converting the products of assimilation into sugar, the so-called chemical rays seem to have a prominent *rôle*.

The results of field experiments showed that sugar production begins at an early stage in the leaves, but is greatest from the beginning of August to the middle of September. Under favourable conditions, there may be a not inconsiderable accumulation of sugar even later.

From the beginning of July, the sum of the percentages of water and sugar in the roots is constant. This, and the fact that the percentage of sugar in the roots increases until the leaves die, indicates that the sugar, once stored in the roots, remains there. It is only when the roots are taken out of the soil and the leaves cut off that the sugar begins to be used up in maintaining the life of the plant and in preparation for second year's growth. N. H. J. M.

**The Carbohydrates of Rye, Barley, and Wheat at Different Periods.** By H. JESSEN-HANSEN (*Bied. Centr.*, 1897, **26**, 630—636; from *Carlsberg. Lab. Meddel.*, 1896, **4**, 145—193).—The grain at the dates on which they were examined had the following weights per 200 (in grams). I. Rye (*a*) 20—22 June, 1893, 2·486; (*b*) 29—30 June, 5·1255; (*c*) 11 July, 9·561, and (*d*) 22 July, 9·505. II. Barley (*a*) 29—30 June, 6·377; (*b*) 3 July, 10·684; (*c*) 14 July, 20·216, and (*d*) 25 July, 19·450. III. Wheat (*a*) 4 July, 5·193; (*b*) 13 July, 9·900, and (*c*) 31 July, 14·300 grams. The following table gives the analytical results at the different dates.

| | Dry matter in fresh grains. | Per cent. in dry substance. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Pentosans. | Starch. | Sol. in 90 per cent. alcohol. | | | Soluble in 70 per cent. alcohol. | | | |
| | | | | Invert-sugar. | Cane-sugar. | ? Secalose. | Invert-sugar. | Cane-sugar. | Baryta prop. | "Unknown." |
| I. *a.* | 27·6 | 5·1 | (11·4)* | 5·15 | 5·23 | 7·78 | 0·90 | 0 | 19·40 | 6·36 |
| *b.* | 33·0 | 7·6 | 34·8 | 3·5 | 2·52 | 1·78 | 0·38 | 0 | 9·62 | 4·82 |
| *c.* | 45·4 | 7·4 | 50·9 | 0·98 | 1·47 | 0·68 | — | 0·50 | 0·11 | 1·68 |
| *d.* | 58·45 | 6·4 | 60·6 | 0·31 | 0·43 | 0·34 | 0·36 | 0·74 | trace | 1·94 |
| II. *a.* | 24·39 | 3·5 | 16·08 | 5·14 | 9·15 | 6·10 | 0·98 | 0 | 9·05 | 7·21 |
| *b.* | 28·60 | 4·1 | 40·40 | 1·84 | 2·74 | 3·03 | 0·67 | 0 | 7·4 | 5·25 |
| *c.* | 40·41 | 5·8 | 57·42 | 0·50 | 0·44 | 0·55 | 0·57 | 0·09 | trace | 1·31 |
| *d.* | 55·60 | 5·7 | 57·57 | — | — | — | 0·68 | 0·47 | 0 | 0·54 |
| III. *a.* | 27·85 | 5·4 | 26·45 | 5·20 | 5·56 | 8·46 | 1·23 | 0 | 6·81 | 4·45 |
| *b.* | 37·77 | 7·0 | 54·45 | 1·14 | 1·27 | 0·71 | 0·36 | 0 | 2·54 | 2·96 |
| *c.* | 55·29 | 6·4 | 65·90 | 0·48 | 0·44 | 0·33 | 0·39 | 0 | trace | 1·15 |

* Determination made in sample taken 20 June, 1894.

The precipitate obtained with baryta from the rye extract yielded a substance, probably identical with Tanret's levosin, which the author terms *apeponin*; this compound has the formula $(C_{12}H_{22}O_{10})_2$, decomposes at 128—130° without discoloration, and melts at about 230°, darkening at the same time. Its specific rotatory power is about $-41·3°$. It does not ferment, and does not reduce alkaline copper solutions.

Barley grain yielded the same constituents as rye, namely, glucose, fructose, cane-sugar and apeponin. Raffinose could not be detected.

In the case of wheat, only the reducing sugars, and apeponin, were identified with certainty.

Oats were also analysed at different dates; but only pentosans and starch were determined. Single grains weighed as follows:—(*a*) 7 July, 17·4; (*b*) 15 July, 34·0; (*c*) 28 July, 51·6, and (*d*) 10 August, 33·8 milligrams. The results were as follows:—

| Dry matter per cent. | | | | Pentosans per cent. in dry matter. | | | | Starch per cent. in dry matter. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *a.* | *b.* | *c.* | *d.* | *a.* | *b.* | *c.* | *d.* | *a.* | *b.* | *c.* | *d.* |
| 41·8 | 36·6 | 52·9 | 84·8 | 27·2 | 19·5 | 11·3 | 12·7 | 2·8 | 11·6 | 40·5 | 42·3 |

Apeponin could not be detected in oats, even at the earlier stages of growth.

N. H. J. M.

**Behaviour of Active Albumin as Reserve Material during Winter and Spring.** By U. Suzuki (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, 3, 253—258).—Daikuhara (Abstr., 1895, 128) showed that the leaves of plants which contain active albumin in the summer, also contain it in October and November, although usually in far less amount.

The examination of the bark and buds (in March, before the buds had opened) of 48 species, showed, in 25 cases, the presence of active albumin; frequently the bark contained more than the buds. Active albumin, therefore, resembles other reserve substances in being stored up in the bark of trees. N. H. J. M.

**Formation of Proteids in Plants by the Reduction of Nitrates.** By EMIL GODLEWSKI (*Ann. Agron.*, 1897, **23**, 310—324; from *Anzeiger Akad. Wiss. Krakau*, 1897, 104—121).—Seedlings of wheat were cultivated in solutions, both with and without nitrate, some in the dark, others exposed to light. The latter were under glass shades through which air free from carbonic anhydride passed. After three weeks, the plants were removed, weighed, dried, and analysed.

There was a loss of dry substance in every case, rather greater in the case of the plants exposed to light than in those grown in darkness. The amount of nitrogen in different forms in the grains and plants (taking the total nitrogen of the seeds as 100) was as follows. (Experiments 1—3 were made in diffused daylight, 4—7 in the dark. 1, 2, 4—6 were supplied with nitrate, 3 and 7 were without nitrate.)

| | Total nitrogen. | Total organic nitrogen. | Nitrogen as proteids. | Soluble proteid nitrogen. | Insoluble proteid nitrogen. | Nitrogen as amides and ammonia. | Nitrogen as nitrates. |
|---|---|---|---|---|---|---|---|
| In seeds | 100 | 100 | 92·68 | 74·04 | 18·64 | 7·32 | 0 |
| 1 with nitrate | 218·72 | 179·97 | 119·14 | 100·19 | 18·95 | 60·83 | 38·75 |
| 2 with nitrate | 206·04 | 149·63 | 108·58 | 90·05 | 18·53 | 41·05 | 56·41 |
| 3 without nitrate | 95 | 95 | 67 | 55 | 12 | 28 | 0 |
| 4 with nitrate | 154·16 | 113·77 | 76·07 | 51·73 | 24·34 | 37·70 | 40·39 |
| 5 with nitrate | 177·11 | 123·26 | 70·75 | 54·53 | 16·22 | 52·51 | 53·85 |
| 6 with nitrate | 174·79 | 122·44 | 71·96 | 55·16 | 16·80 | 50·48 | 52·35 |
| 7 without nitrate | 92·73 | 92·73 | 61·67 | 45·05 | 16·62 | 31·06 | 0 |

The results show that, both in diffused daylight and in absence of light, the plants accumulated considerable amounts of nitrates. Proteids were produced, under the influence of light, when nitrates were supplied; in the dark, formation of proteids from nitrates did not take place to any extent, if at all. Proteids are not formed directly from nitrates; non-proteid compounds are first produced which are subsequently converted into proteids, these non-proteid compounds being formed both with and without the aid of light, and in much greater quantity when nitrate is supplied than without nitrate. Light is necessary for their transformation into proteids. (Compare Laurent, Marchal, and Carpiaux, *Bul. Acad. roy. Belg.*, [iii], **32**, 816—865; and Hansteen, *Ber. deut. bot. Ges.*, 1896, **14**, 362.) N. H. J. M.

**A Compound rich in Manganese obtained from Woody Tissue.** By GABRIEL GUÉRIN (*Compt. rend.*, 1897, **125**, 311—312).—When wood sawdust is macerated for two or three days with a 1 per cent. solution of potassium hydroxide, a deep brown liquid is obtained, and when this is acidified with hydrochloric acid, a bulky, flocculent precipitate is produced. This precipitate can be washed with very dilute hydrochloric acid, redissolved in ammonia, reprecipitated by acid, washed and dried. It is a pale brown powder, which, when

obtained from the beech, had the composition, C, 52·762; H, 5·04; N, 4·60; S, 0·666; P, 1·297; Mn, 0·402 per cent. C. H. B.

**Volatile Reducing Substance of the Green Parts of Plants.** By THEODOR CURTIUS and J. REINKE (*Bied. Centr.*, 1897, **26**, 573; from *Ber. deut. bot. Ges.*, 1897, 201, and *Rep. Chem. Ztg.*, 1897, 133).—In accordance with Baeyer's theory, Reinke detected, some years ago, an aldehydic substance in chlorophyllous plants which does not occur in fungi.

By distilling leaves with steam, and treating the distillate with a hot, saturated alcoholic solution of metanitrobenzhydrazide, a small quantity of flakes of a microcrystalline precipitate was obtained. This compound of an aldehyde alcohol with 1 mol. nitrobenzhydrazide, is soluble in water, and readily soluble in cold absolute alcohol; the *aldehyde alcohol* itself, $C_7H_{11}O \cdot CHO$, is supposed to be the reducing substance of green leaves. N. H. J. M.

**Production of Ammonia from Vegetable Substances and Humus.** By ÉMILE BRÉAL (*Ann. Agron.*, 1897, **23**, 356—369).—Nettles kept for three hours in carbonic anhydride, and then distilled with magnesia, yielded ammonia, whilst a similar plant which had been kept in air did not. Ammonia was also obtained from clover and lucerne, and from maize after treatment with chloroform or ether; vegetable substances, when dried in confined air, likewise yielded ammonia.

*Poa annua*, when kept in water covered with a shade through which air was passed, did not give off ammonia, but the same plant, after the roots were cut off, yielded ammonia in the course of 24 hours. The water in which vegetable matter has been kept is capable of inducing ammonia production from other substances, such as wool, horn, leather, &c. Soil humus gives off ammonia after contact with a leaf taken from a fermenting vegetable infusion.

Plants may induce the production of ammonia in the soil in contact with their roots, and absorb the ammonia thus liberated. N. H. J. M.

**Occurrence of Amines in the Juice of the Sugar-Cane.** By J. L. BEESON (*J. Amer. Chem. Soc.*, 1896, **18**, 743—744).—Although the products of the sugar-beet have long been known to contain amines, their presence in the juice of the sugar-cane has not hitherto been recognised. By heating the precipitate formed on adding lime water to sugar-cane juice, the author has obtained a product which possesses the general properties of an amine. E. W. W.

**Bisabol-Myrrha.** By W. TUCHOLKA (*Arch. Pharm.*, 1897, **235**, 289—301).—An analysis of bisabol-myrrha obtained from Somaliland gave the following results. Gum soluble in water, 22·1; gum soluble in soda, 29·85; resin, 21·5; bitter principles, 1·5; ethereal oil, 7·8; water, 3·17; and inorganic matter, &c., 13·4 per cent. The ethereal oil, when dissolved in ether and saturated with gaseous hydrogen chloride, yielded a dextrorotatory compound of the formula $2(C_{10}H_{16},2HCl)$, forming hexagonal plates, and melting at 79·2°. This, on treatment with anhydrous sodium acetate and glacial acetic acid, gave the *hydrocarbon*, $C_{10}H_{16}$, having a sp. gr. = 0·8914 at 17°, a refraction $n_D' = 1·4608$ at 17°, and a dispersion = 0·01186 at 17°; the molecular

refraction therefore $=44 \cdot 17$, from which it appears that the compound contains two double bonds. An oil boiling at 230—231°, and of the formula $C_{56}H_{96}O$ was isolated from the residue after treating it with hydrogen chloride; the matter is still under investigation.

J. F. T.

**Physiological Action of Disodium Sulphite on Phænogams.** By K. NEGAMI (*Bul. Coll. Agric. Imp. Univ. Tokyo*, 1897, **3**, 259—264).—The fact that amidosulphonic acid is innocuous to lower vegetable and animal life, but poisonous to phænogams (this vol., ii, 279) suggested the possibility that the effect on the latter might be due to the production of sulphurous acid.

Experiments in which onion and barley plants, branches of *Prunus Persica* and *P. triflora*, leaves of *Heliotropium Peruvianum* and *Vitis incrustans*, and seeds of radish, barley and soja bean were subjected to the action of disodium sulphite (1 per cent.) showed that the salt is poisonous to the developed plants but does not injure radish and barley seeds. The germination of soja bean was, however, very much retarded, possibly owing to the oxygen dissolved in the water being absorbed by the sulphite. Further experiments will have to be made to decide whether the action of the sulphite accounts for the injurious effect of amidosulphonic acid. N. H. J. M.

**Poisonous Action of Ammonium Salts on Plants.** By S. TAKABAYASHI (*Bul. Coll. Agric. Imp. Univ. Tokyo*, 1897, **3**, 265—274).—Many plants develop better when manured with nitrates than with ammonium salts, and whilst nitrates may be stored up in plants to a considerable extent, ammonium salts are not, most of the excess being converted into asparagine (Kinoshita, Abstr., 1896, ii, 54).

Ammonium carbonate (0·5 per cent.) kills vegetable objects in a few days, and 0·05 per cent. solutions have the same effect but more slowly. Whilst the poisonous effect of the stronger solution cannot be counteracted, the noxious effect of the weaker solution can be retarded, in many cases, by the presence of cane-sugar or glycerol. Ammonium sulphate is much less poisonous than the carbonate.

Two sets of barley plants (one of which had been exhausted of reserve material, and the other kept in direct sunlight in 1 per cent. cane-sugar) were placed in solutions of (1) ammonium carbonate, (2) ammonium chloride, (3) ammonium sulphate, and (for control) (4) sodium carbonate, (5) sodium chloride, and (6) water; the solutions were of two degrees of strength, 0·1 and 0·5 per cent. During the experiment, the plants were kept in the dark. A second and third series of experiments included onions and wheat respectively, as well as barley.

The results confirmed the poisonous effect of ammonium salts in absence of sufficient sugar in the plant. In well-nourished plants, the noxious effect of ammonium salts is not noticed, owing to their conversion into asparagine. N. H. J. M.

**Injury to Rye by Perchlorate contained in Nitrates.** By By B. SJOLLEMA (*Ann. Agron.*, 1897, **23**, 328—329; from *Deut.*

*landw. Presse.*, 1897, No. 3).—In Holland and Belgium, rye crops which had been manured with sodium nitrate were more or less damaged. In some cases, the plants, after a few weeks, seemed scorched; in other cases, where the injury was less, the growth was stunted and seed production imperfect. A number of samples of the nitrate were examined and found to contain from 0·14 to 6·79 per cent. of perchlorate, and nearly corresponding amounts of potash. Direct experiments with sodium and potassium perchlorates showed that these salts retard germination and cause the leaves of plants to which they were applied to become yellow.

It is concluded that 200 kilos. of sodium nitrate (? per hectare) containing 0·5 per cent. of perchlorate would be injurious.

Dehérain mentions that Muntz (*Ann. Chim. Phys.*, [vi], **11**, 111; and Abstr., 1895, 870) showed that iodides and bromides are oxidised by nitrifying organisms to iodates and bromates respectively, whilst attempts to convert chlorides into chlorates failed. It is still unknown whether the perchlorates found in sodium nitrate could have been produced by micro-organisms. N. H. J. M.

**Nitrogen Nutrition of the Leguminosæ.** By KARL VON ROZDEJCZER (*Inaug. Diss. Leipzig*).—Peas were grown in sandy soil (N = 0·0128 per cent.), in loamy soil (N = 0·122), and in humus soil (N = 0·214 per cent.), in pots containing respectively 18·66, 14·66, and 12·82 kilograms of dry soil. There were three series of experiments, (1) unmanured, (2) with minerals and sodium nitrate (N = 0·3048 gram per pot), and (3) with minerals alone. The pots were in the open air except in very wet weather, and the amount of nitrogen in the rain and in the water used was determined; there were three or four plants to each pot. On taking up the plants, the greatest nodule development was found in the pots which had received mineral manure, and in the unmanured sandy soil; the development was only slight in the loamy and humus soils, and very slight under the influence of sodium nitrate. The following summary shows the average amount of nitrogen (in grams) per pot, in the seeds sown in the soil, and in the produce, and also the gain or loss at the end of the experiment.

| | | | | In soil. | | | | Total. | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Pots. | | | | Initial.* | Final. | In seed. | In produce. | Initial. | Final. | Gain or loss. |
| 1—3 | Sandy | soil; | no manure... | 2·4333 | 2·4342 | 0·0321 | 0·2544 | 2·4654 | 2·6886 | 0·2232 |
| 8, 9, 11 | ,, | ,, | sod. nitrate | 2·7381 | 2·4656 | 0·0321 | 0·3744 | 2·7702 | 2·8400 | 0·0698 |
| 15—17 | ,, | ,, | minerals...... | 2·4333 | 2·4342 | 0·0370 | 0·3680 | 2·4703 | 2·8022 | 0·3319 |
| 4, 6 | Loamy | ,, | no manure... | 18·1838 | 18·0914 | 0·0370 | 0·3222 | 18·2208 | 18·4136 | 0·1928 |
| 10, 12 | ,, | ,, | sod. nitrate | 18·4886 | 18·0914 | 0·0407 | 0·4148 | 18·5293 | 18·5062 | −0·0231 |
| 5, 7 | Humus | ,, | no manure... | 28·0520 | 27·9690 | 0·0333 | 0·4965 | 28·0853 | 28·4650 | 0·3797 |
| 13, 14 | ,, | ,, | sod. nitrate | 28·3568 | 28·0995 | 0·0333 | 0·3375 | 28·3901 | 28·4370 | 0·0469 |

The results show a gain of nitrogen in each set, except in the case of the loamy soil which received nitrate, and in this there was a loss; the loss was in pot 10; in pot 12, there was a gain of nitrogen (= 0·0276).

It is concluded that, with insufficient nitrogen in the soil, peas assimilate considerable amounts of free nitrogen, and thus enrich the soil; but with increased supply of soil nitrogen, this power of fixing free nitrogen diminishes, the plant utilising the combined nitrogen of the

* Including 0·018 gram in rain, and (Pots 8—14) 0·3048 gram as nitrate.

soil. With rich soil, elementary nitrogen is either not utilised at all or else in very small quantities. Leguminous crops should be well manured with potash and phosphoric acid. N. H. J. M.

**The Amount of Nitrogen conveyed by Red Clover to Different Kinds of Soil.** By NAPOLEONE PASSERINI (*Bol. Scuola Agrar. Scandicci*, 1895, **3**, 102—111).—Red clover was grown in three different soils contained in wooden boxes 50 cm. square. The soil had the following composition (per cent. in dry soil).

| | Sand. | Clay. | Loss on heating. | $CaCO_3$. | N. |
|---|---|---|---|---|---|
| 1. | 54·542 | 34·670 | 6·800 | 1·581 | 0·1546 |
| 2. | 85·406 | 10·528 | 3·386 | 0·323 | 0·1033 |
| 3. | 40·936 | 36·180 | 9·818 | 13·152 | 0·1366 |

Calcium phosphate and sulphate, and potassium chloride were mixed with the soil, each at the rate of 400 kilograms per hectare. Two crops of clover were cut weighing together (1) 223, (2) 312, and (3) 252 grams respectively; or as hay, 39·5, 69, and 76 grams.

At the conclusion of the experiment, the nitrogen of the soil was again determined, with the following results. Nitrogen, in dry soil =(1) 0·1388, (2) 0·0847, and (3) 0·1600 per cent. The total loss or gain of nitrogen is shown below (in grams).

| | N. in soil. | | | | | Total N. | | |
|---|---|---|---|---|---|---|---|---|
| | Initial. | Final. | Difference. | N. in seed. | N. in crop. | Initial. | Final. | Loss or gain. |
| 1. | 167·673 | 150·537 | −17·136 | 0·0237 | 1·2897 | 167·6967 | 151·8267 | −17·1590 |
| 2. | 137·969 | 113·126 | −24·843 | 0·0237 | 2·1411 | 137·9922 | 115·2671 | −24·8662 |
| 3. | 151·978 | 178·013 | +26·035 | 0·0237 | 2·4287 | 152·0021 | 180·4417 | +26·0109 |

Whilst there was a gain in the calcareous soil (3), under the influence of red clover, in the other two soils there was an actual loss, due in part to the loss of nitrates in drainage, and partly to less active fixation of nitrogen. The results indicate that "sideration" will not be successful in soil poor in lime, even when manured with phosphates and potassium salts. N. H. J. M.

**Experiments on the Effect of Magnesia on Wheat.** By NAPOLEONE PASSERINI (*Bol. Scuola Agrar. Scandicci*, 1895, **3**, 140—142).—Wheat was sown in three plots of 10 square metres, and manured in the autumn with mineral phosphates, and in the spring with sodium nitrate (80 kilograms per hectare). Magnesium carbonate was applied in quantities of 500 and 200 kilograms per hectare to plots 1 and 2 respectively, whilst none was given to plot 3. The following amounts of produce were obtained (kilograms per hectare).

| 1. $MgCO_3$, 500 kilos. | | 1. $MgCO_3$, 200 kilos. | | 3. Without $MgCO_3$. | |
|---|---|---|---|---|---|
| Grain | Straw and chaff. | Grain | Straw and chaff. | Grain | Straw and chaff. |
| 1,900 | 10,100 | 2,180 | 9,320 | 2,320 | 9,680 |

The presence of magnesium carbonate, in the quantities applied, caused, therefore, a diminished yield of grain. The quality of the grain was also injured, the weight per litre in the three experiments

being respectively (1) 766, (2) 770, and (3) 777 grams. (Compare Larbalétrier and Malpeaux, Abstr., 1896, ii, 445.) N. H. J. M.

**The Pentosans and Crude Fibre of Various Foods.** By FRANZ DÜRING (*Bied. Centr.*, 1897, **26**, 603—605; from *J. Landw.*, 1897, **45**, 79).—The following results are given (per cent. in dry matter).

| — | Crude protein $N \times 6.25$. | Ether extract. | Ash. | Crude fibre (free from pentosans). | N-free extract (free from pentosans). | Pentosans. Furfuraldehyde $\times 1.84$. | Dry matter. |
|---|---|---|---|---|---|---|---|
| Meadow hay ... | 11·70 | 3·60 | 7·03 | 21·09 | 37·63 | 18·95 | 93·26 |
| Rye straw ...... | 3·24 | 2·28 | 4·31 | 37·61 | 23·47 | 29·09 | 93·20 |
| Clover hay ...... | 13·90 | 2·31 | 6·01 | 33·74 | 28·00 | 16·04 | 92·04 |
| Lupin straw . .. | 5·80 | 1·36 | 3·76 | 45·34 | 22·91 | 20·83 | 91·56 |
| Sheep fæces .... | 11·89 | 4·80 | 12·79 | 21·16 | 29·14 | 20·22 | 92·80 |

The results support the view of Pfeiffer and Götz (this vol., ii, 428) that, in herbivorous animals, hippuric acid is derived from pentosans, and this also accords with the observed increased amount of hippuric acid after feeding with oats and oat straw, as compared with food consisting essentially of leguminous corn or straw. N. H. J. M.

**Nitrification in Soil.** By R. BURRI and ALBERT STUTZER (*Chem. Centr.*, 1896, ii, 113; from *Centr. Bakt. Par.*, **2**, ii, 196—204).—All cultivations which oxidised ammonia to nitrite, contained an organism greatly resembling Winogradsky's *Nitrosomas europæa*, but attempts to obtain pure cultivations on silicic acid plates failed. With regard to the oxidising power of nitrous organisms from different sources (five were from Germany and one from Africa), there seems to be no essential difference. A nitric organism was obtained from Northeim soil which was identical with that obtained by Winogradsky from Quito; when cultivated on gelatin, this organism no longer oxidised nitrites, and only occasionally recovered its nitrifying power when recultivated in mineral matter.

Cultivations containing both nitrous and nitric organisms could be made, by appropriate addition of nitrogenous salts, to nitrify like soil, that is, to apparently produce nitrates directly from ammonia.

N. H. J. M.

**Nitrification of the Nitrogenous Matter of Soil and of some Nitrogenous Manures.** By PH. BONAME (*Mauritius Rapp. Ann. Stat. Agron.*, 1896).—The soil with which the experiments were made consisted of coarse sand, 2·8; fine sand, 46·3; and clay, 25·5 per cent., with a trace of humus, and contained N = 0·350, CaO = 0·155, and MgO = 0·043 per cent. It is considered a fair sample of the soil of the island where high percentage of nitrogen with low percentage of lime is common.

A number of metallic cylinders were filled with the soil (3 kilograms), (1) alone, and mixed with (2) ammonium sulphate, (3) dried blood, (4) cake, and (5) fish guano respectively. The amount of

nitrogen applied was the same in each case, and amounted to 0·180 per cent. of the soil. There were two cylinders in each experiment, one of which received 5 per cent. of chalk ("sable calcaire" containing $CaCO_3$, 91·1; $CaSO_4$, 0·68; insoluble matter, 1·12; and water, $Na_2O$, $MgO$, &c., 7·10 per cent.).

The following table shows the amounts of nitrogen, per million of soil, as ammonia and as nitrites, at the different dates. The experiment commenced 15 April. The numbers 1—5 represent the cylinders without, 1*a*—4*a* the cylinders with chalk, 1*b* was soil to which lime but no nitrogenous manure was added.

| | N as $NH_3$ per million. | | | | | | N as $N_2O_5$ per million. | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 11 June. | 12 July. | 14 Aug. | 15 Sept. | 26 Nov. | 20 Feb. | 11 June. | 12 July. | 14 Aug. | 15 Sept. | 26 Nov. | 20 Feb. |
| 1 | 5 | 17 | 18 | 25 | 29 | — | 42 | 50 | 83 | 83 | 80 | 80 |
| 1*a* | 25 | 30 | 25 | 18 | 28 | — | 62 | 73 | 60 | 100 | 100 | 110 |
| 1*b* | 22 | 46 | 80 | 16 | 35 | — | 170 | 200 | 190 | 240 | 280 | 280 |
| 2 | 1610 | 1650 | 1540 | 1500 | 1450 | 1040 | 220 | 290 | 350 | 440 | 510 | 850 |
| 2*a* | 1020 | 530 | 80 | 40 | 70 | 50 | 750 | 1330 | 1860 | 1900 | 1870 | 1880 |
| 3 | 710 | 730 | 680 | 630 | 510 | 500 | 660 | 740 | 850 | 880 | 1010 | 1010 |
| 3*a* | 200 | 70 | 40 | 40 | 30 | 50 | 1230 | 1510 | 1590 | 1580 | 1740 | 1780 |
| 4 | 630 | 550 | 480 | 470 | 130 | 40 | 590 | 820 | 950 | 1010 | 1390 | 1550 |
| 4*a* | 260 | 60 | 70 | 20 | 40 | 30 | 970 | 1390 | 1370 | 1480 | 1550 | 1660 |
| 5 | 550 | 400 | 300 | 180 | 40 | — | 740 | 1100 | 1130 | 1370 | 1610 | 1640 |

The results show a very marked effect produced by chalk on the rate of nitrification, whilst lime, in No. 1*b*, had a still greater effect, although applied in much smaller quantity (1 per cent.). The better results obtained with lime are partly ascribed to its being in a finer state of division than the chalk. Ammonium sulphate nitrified very slowly in absence of chalk, but the addition of chalk to the otherwise unmanured soil did not have much effect on nitrification. Fish nitrified most readily, then cake, dried blood, and ammonium sulphate; probably nitrification is assisted by the presence of calcium phosphate and carbonate in the organic manures. The slow nitrification of ammonium sulphate, and the beneficial results obtained by its application to crops, support the view that, under some conditions, plants may directly utilise ammonium salts.

In another series of experiments, it was found that, with dried blood, with and without chalk, the soil-extracts contained, with chalk, 481 parts of lime and 30 parts of magnesia; without chalk, only 201 and 65 parts of lime and magnesia respectively per 1,000 parts of nitric acid. As, to produce calcium nitrate, 518 parts of lime would be necessary, it is concluded that the excess of nitric acid is present as ammonium salt.

The temperature of Mauritius is favourable to nitrification, the

mean daily temperature of the year being 59° to 90°; and during the warm season, December to June or July, the soil is also sufficiently moist. N. H. J. M.

**Fixation and Nitrification of Nitrogen in Arable Soils.** By PIERRE PAUL DEHÉRAIN (*Compt. rend.*, 1897, **125**, 278—283).—Arable soil was kept moist and protected from frost, and it was found that, under these conditions, there is not only rapid nitrification even during the winter months, but also a considerable increase in the total nitrogen. In one set of experiments, carried on from November, 1896, to June, 1897, the nitric nitrogen increased from 0·0 gram to 0·390 gram per kilogram, the organic nitrogen from 1·720 to 1·900, and the total nitrogen from 1·720 to 2·290 grams per kilogram. The simultaneous occurrence of rapid nitrification and considerable fixation of atmospheric nitrogen is very noteworthy.

Slow drying of the soil is, as a rule, inimical to nitrification, but the magnitude of the effect varies greatly with different soils; the rapid desiccation that takes place during a drought is, however, almost always decidedly injurious. The conditions most favourable to nitrification and the fixation of atmospheric nitrogen seem to be the maintenance of an equable temperature and a somewhat high degree of humidity. C. H. B.

**Increase of the Nitrogen of the Soil by White Mustard.** By STANISLAUS VON KOWERSKI (*Inaug. Diss. Halle a. S.*, 1895).—A number of pot experiments were made, in which white mustard was grown in two lots of arable soil, containing respectively 0·1149 and 0·1261 per cent. of nitrogen; there were also two pots with mustard and peas together, as in Liebscher's experiments (Abstr., 1894, ii, 201). The pots held about 14 kilograms of soil, containing about 16 grams of nitrogen. The soil of six of the pots was sterilised, but no attempt was made to maintain sterilisation, and the whole experiment was conducted out of doors. Most of the pots received sodium nitrate ($N = 0·5306$ and 0·849 gram per pot) as well as mineral manure. Each pot showed a gain of nitrogen, the gain being 2 to 7 times greater in the unsterilised than in the sterilised soil; there was also a greater gain of nitrogen under the influence of nitrogenous manure than when unmanured.

It is concluded that the fixation of free nitrogen took place under the influence of micro-organisms present in the soil, and that the activity of the microbes is assisted both by sodium nitrate and, in rich soil, by vigorous vegetation (such as mustard) which would prevent the microbes becoming injured by excess of combined nitrogen.

White mustard does not itself assimilate elementary nitrogen. Peas growing in rich soil, which only reach the flowering period, do not assimilate free nitrogen even when their roots have nodules.

N. H. J. M.

**Conservation of Farmyard Manure.** By FRANZ W. DAFERT and R. BOLLIGER (*Rel. Ann. Inst. Agron. Est. São Paulo, Campinas*, 1894—1895, **7** and **8**, 175—186).—The object of the experiments was to ascertain the effect of the amount of moisture on the amount of nitrogen

and organic matter of stable manure both with and without addition of gypsum.

Known amounts (about 400 grams) of ass-manure, without and with gypsum (5 per cent.), were kept in cylindrical vessels in the shade, and the amounts of dry matter and nitrogen determined after intervals of 92, 106, 120, and 134 days. At the commencement, the manure contained 22·20 per cent. of dry matter; in the "dry" experiments, the percentage of dry matter rose to 45·9 without, and 69·5 with gypsum, whilst in the "wet" experiments the percentage was maintained at about 12 and 17 respectively. The following numbers show the percentage loss or gain of dry matter and nitrogen during the successive periods.

| | Loss of dry substance (per cent.). | | | | Loss of nitrogen (per cent. of total). | | | |
|---|---|---|---|---|---|---|---|---|
| | 92 days. | 106 days. | 120 days. | 134 days. | 92 days. | 106 days. | 120 days. | 134 days. |
| Dry: without gypsum ... | 42·72 | 6·42 | 3·72 | 2·28 | 11·16 | 2·13 | 0·35 | 0·61 |
| Moist: " " ... | 45·05 | 2·70 | 0·84 | 0·08 | 15·54 | 13·04 | 2·31 | 0·10 |
| Dry: with " ... | 31·38 | 7·60 | 5·45 | 6·30 | 6·89 | +0·17 | +0·18 | +2·76 |
| Moist: " " ... | 38·55 | 2·38 | 0·79 | 0·08 | 8·95 | 7·49 | 1·40 | 4·80 |

It is concluded that the decomposition of manure depends largely on temperature and moisture, a difference of 1°, and of 1 per cent. of water, having a distinct influence. At the commencement, the decomposition of organic matter predominates, whilst the breaking up of nitrogenous compounds follows later. Gypsum, when well mixed with the manure, prevents loss of organic matter and nitrogen. During the first period, dryness favours the preservation of organic matter (yielding inferior manure), whilst moisture (within limits) assists the preservation of the nitrogen, producing manure of good quality. In the second period, excess of water is injurious.

Under certain conditions, not yet understood, there was a gain of nitrogen. N. H. J. M.

**Drainage Waters.** By Pierre P. Dehérain (*Ann. Agron.*, 1897, **23**, 241—267. Compare Abstr., 1895, ii, 458).—*Results obtained, March*, 1895—*March*, 1896.—The rainfall of this year was nearly equally distributed between the winter and summer months. There was no drainage during the summer through any of the cases. In the spring (May 9), drainage was collected from the fallow cases (1, 12, 13, and 14) and from those planted with vines. The average amount from the fallow cases was 10·1 millimetres (= 0·40 inch), and it contained nitrogen as nitrates corresponding with 9·38 kilograms per hectare (= 8·38 lbs. per acre). From the vine cases, the drainage was less than 1 millimetre, and the loss of nitrogen only 1·195 kilograms per hectare (= 1·07 lbs. per acre). During the winter months, the fallow cases yielded drainage: average of 1 and 13 (not dug) = 72·1 millimetres (2·84 inches), of 12 and 13 (dug) 89·45 millimetres (3·52 inches). The average loss of nitrogen in 1 and 13, and in 12 and 13 respectively was 82·5 kilograms (73·7 lbs. per acre), and 118·68 kilograms per hectare (105·9 lbs. per acre). The character of the produce from the various cases is described, and the amounts given.

*Results obtained, March* 1896—*March* 1897.—The rainfall of this year was below the average during the early part of the year, but exceptionally high in September and October, making the total amount for the year above the average. The winter was mild. The following table shows the amount of drainage during the year from each case, the amount of produce, and the loss of nitrogen as nitrates in the drainage.

| Produce in kilograms per hectare and lbs. per acre. | Drainage. | | Nitrogen as nitrates. | | |
|---|---|---|---|---|---|
| | Mm. | Inches. | Per million. | Kilos. per hectare. | Lbs. per acre. |
| 1. Fallow—not dug | 282 | 11·11 | 0·074 | 209·1 | 186·7 |
| 2. Rye grass, 5,325 kilos. = 4,754 lbs. | 198 | 7·80 | 0·0013 | 2·6 | 2·3 |
| 3. Oats, grain, 19·5 q. met. = 1,741 lbs.; straw, 45·2 q. m. = 4,036 lbs. | 185 | 7·29 | 0·0044 | 8·3 | 7·4 |
| 4. Oats, grain, 18·3 q. met. = 1,634 lbs.; straw, 42·5 q. m. = 3,794 lbs. | 201 | 7·92 | 0·007 | 14·2 | 12·7 |
| 5. Oats, grain, 18·3 q. met. = 1,634 lbs.; straw, 42·5 q. m. = 3,794 lbs. | 204 | 8·04 | 0·013 | 26·2 | 23·4 |
| 6. Maize: green fodder = 70,000 kilos. = 62,500 lbs. | 176 | 6·93 | 0·014 | 24·2 | 21·6 |
| 7. Maize: green fodder = 71,250 kilos. = 63,616 lbs. | 169 | 6·66 | 0·009 | 16·5 | 14·7 |
| 8. Maize: green fodder = 75,000 kilos. = 66,964 lbs. | 167 | 6·58 | 0·018 | 28·7 | 25·6 |
| 9. Wheat: Vetches: grain = 20·75 q. = 1,853 lbs.; straw, 42·5 q. = 3,794 lbs.; vetches = 7,500 k. = 6,696 lbs. | 168 | 6·62 | 0·009 | 14·4 | 12·8 |
| 10. Wheat: grain = 20·2 q. = 1,803 lbs.; straw, 42·75 q. = 3,817 lbs. | 190 | 7·49 | 0·017 | 33·3 | 29·7 |
| 11. Wheat: Vetches: grain = 16·0 q. = 1,429 lbs.; straw, 42·5 q. = 3,794 lbs.; vetches = 6,500 k. = 5,803 lbs. | 174 | 6·86 | 0·005 | 7·9 | 7·1 |
| 12. Fallow—dug | 293 | 11·54 | 0·075 | 220·2 | 196·4 |
| 13. ,, not dug | 283 | 11·15 | 0·062 | 176·9 | 157·9 |
| 14. ,, dug and rolled | 285 | 11·23 | 0·072 | 205·2 | 183·2 |
| 15. Potatoes: tubers, 27,500 kilos. = 24,553 lbs. | 148 | 5·83 | 0·014 | 27·7 | 24·7 |
| 16. Vines: vintage, 18,800 kilos. = 16,786 lbs. | 189 | 7·45 | 0·022 | 40·8 | 36·4 |
| 17. Vines: vintage, 18,950 kilos. = 16,920 lbs. | 188 | 7·41 | 0·045 | 84·0 | 75·0 |
| 18. Sugar beet: roots, 28,000 kilos. = 25,000 lbs. | 182 | 7·17 | 0·0014 | 2·7 | 2·4 |
| 19. Sugar beet: roots, 32,750 kilos. = 29,241 lbs. | 182 | 7·17 | 0·0002 | 0·3 | 0·3 |
| 20. Sugar beet: roots, 31,250 kilos. = 27,902 lbs. | 194 | 7·64 | 0·0003 | 0·5 | 0·4 |

In 1895, the crops were, in cases 3 to 5, potatoes; 6 to 8, clover; 9 to 11, beet; 15, oats; 18 to 20, wheat, the other cases being the same as in 1896. No manure was applied.

The results of the experiments show, not only an enormous excess

in loss of nitrogen in the fallow cases as compared with the cases covered with vegetation, but that, supposing the whole of the nitrogen in the plants to have been taken up in the form of nitrates, the nitrogen of the crops and of the corresponding drainage may amount to less than that of the drainage from fallow land. In case 10, for instance, the total produce, straw and grain, is estimated to contain 61 kilograms of nitrogen per hectare (54·5 lbs. per acre), which, added to the nitrogen found in the drainage, makes 94 kilograms (84 lbs. per acre). In the fallow cases, the loss amounted to about 200 kilograms (180 lbs. per acre). This difference is ascribed to deficiency of rain in April and May, in consequence of which the soil bearing vegetation would become too dry for active nitrification, whilst the fallow soil would still retain sufficient moisture. When rain is abundant during the period of active vegetation, the nitrogen of the crop added to that lost in the drainage corresponds more nearly with the nitrogen lost in bare soil. This is illustrated by the results obtained with maize, which developed later; the total produce is estimated to contain 174 kilograms of nitrogen per hectare, which, when added to the loss in drainage, makes 197 kilograms.

The Grignon soil, when moist, is capable of yielding sufficient nitrates for the heaviest crops. By means of irrigation in the spring, increased nitrification could be induced and a great saving of nitrogenous manures effected.

Léon Martin (*ibid.*, 276—277) refers to the exceptionally wet winter, and the consequent loss of nitrates, which he supposes to be the cause of the unpromising appearance of the wheat crop (in May), and states that the power which straw has of retaining nutritive matters is of great value in wet seasons. He suggests that it would be of interest to ascertain the amount of nitrates lost by drainage in soils to which farmyard manure and mineral manures respectively had been applied.

Dehérain in reply (*ibid.*, 277—279), points out the importance of occupying the land as much as possible to avoid excessive drainage. It is doubtful whether the yellow appearance of the wheat was due to excess of water in the soil, experiments having shown that soil, during frequent rains, may contain less water after than before the showers. This is because the spaces between the particles of soil become less during rain. It is for this reason that the drainage through the cases is sometimes in excess of the rainfall.

Application of farmyard manure does not always render soil better able to retain water. At Grignon, soil thus manured gave slightly more drainage than the unmanured soil. N. H. J. M.

---

## Analytical Chemistry.

---

**Titration with Potassium Hydrogen Carbonate.** By Georges Freyss (*Chem. Centr.* 1896, ii, 511; from *Bull. Soc. Ind. Mulhouse*, **66**, 250—254).—This salt, being anhydrous and easily obtained in a

pure state, offers special advantages in volumetric analysis. A standard solution is made by dissolving 100 grams of the salt and making up to 1 litre.

To estimate the amount of caustic alkali in the presence of a carbonate, an excess of barium chloride is first added, and the standard solution is then run in until the red colour disappears, using phenolphthalein as indicator. To estimate bicarbonate in the presence of normal carbonate, a definite quantity of normal potash is first added, and the excess is then titrated as directed.

The solution may be used for determining the amount of alkali necessary to dissolve the phenols in tar-oil, or the phenolic compounds in essential oils. Normal soda is first prepared, using water previously saturated with phenols similar to those to be tested. Twenty grams of the tar-oil is agitated with 250 c.c. of the specially prepared normal soda, allowed to stand for a time, and then the aqueous layer is measured and drawn off. After clarifying with a little calcium carbonate, the liquid is filtered without delay, and in one-half of the filtrate the excess of alkali is titrated by simply adding normal potassium hydrogen carbonate until the liquid gets turbid. L. DE K.

**Separation of Chlorine and Bromine in the Presence of Acetates, Sulphates, and Nitrates.** By PAUL EHRHARDT JANNASCH and E. KÖLITZ (*Zeit. anorg. Chem.*, 1897, **15**, 66—67).—When the method for the direct separation of chlorine and bromine by means of potassium permanganate in strong acetic acid solution is employed, it is essential that acetates should not be present, as they retain the greater portion of the bromine. The presence of sulphates or nitrates is without influence on the reaction. Therefore, when the halogens are present in alkaline solutions, these must be neutralised or made faintly acid with sulphuric or nitric acid, but never with acetic acid. E. C. R.

**Separation of Chlorine, Bromine, and Iodine in the Analysis of Organic Compounds.** By PAUL EHRHARDT JANNASCH and E. KÖLITZ (*Zeit. anorg. Chem.*, 1897, **15**, 68—70).—The mixed halogens are obtained as silver salts either by Carius's method or by combustion of the organic compound with lime. The precipitate is then fused with pure sodium hydroxide in a silver crucible, the melt extracted with water, and the filtrate from the metallic silver, after being made slightly acid with sulphuric or nitric acid, is distilled with permanganate and acetic acid. E. C. R.

**Estimation of Sulphur in Pig Iron.** By ANDREW A. BLAIR (*J. Amer. Chem. Soc.*, 1897, **19**, 114—115).—The author and others find that there is a class of pig-irons in which the sulphur is evolved but incompletely as hydrogen sulphide when the sample is dissolved in hydrochloric acid, and that the residue is not oxidised by nitric acid, or even by aqua regia.

To estimate the total sulphur, Bamber's process is recommended. Five grams of the sample is dissolved in strong nitric acid; from 2 to 5 grams of nitre is added, the whole evaporated to dryness in a platinum dish, and the residue ignited. The product is then boiled with a weak

solution of sodium carbonate, and the sulphuric acid estimated in the filtrate with the usual precautions. L. DE K.

**Estimation of Sulphur in Iron Pyrites or Native Zinc Sulphides.** By A. NOAILLON (*Zeit. angw. Chem.*, 1897, 351—352).—The author has worked out a process by which all danger of losing sulphuric acid by evaporation is removed.

1·25 grams of the powdered material is treated with a mixture of 10 c.c. of nitric acid of sp. gr. 1·4, and 10 c.c. of a 30 per cent. solution of sodium chlorate; oxidation takes place rapidly in the cold. Excess of hydrochloric acid is then added, the mixture evaporated to dryness on a sand bath, the residue taken up with dilute hydrochloric acid, and the solution precipitated, while hot, with a slight excess of ammonia. When cold, the whole is made up to exactly 500 c.c. and then filtered. Two hundred c.c. of the filtrate, representing 0·5 gram of the sample, is then boiled to expel the ammonia, and after adding a slight excess of hydrochloric acid the sulphuric acid is estimated as barium sulphate.

L. DE K.

**Estimation of Sulphur in Petroleum.** By AUFRECHT (*Chem. Centr.*, 1896, ii, 361; from *Pharm. Zeit.*, **41**, 469).—Fifty c.c. of the sample is mixed with 0·5 gram of sodium hydrogen carbonate and submitted to distillation until only 5 c.c. is left in the retort. The residue is then transferred by means of ether to a large porcelain dish, and when the ether has volatilised another 0·5 gram of soda is added and the whole evaporated; finally, the residue is ignited with gradual addition of ammonium nitrate until the ash is quite white. The sulphuric acid derived from the sulphur in the sample is then estimated as usual. L. DE K.

**Estimation of Sulphur in Coke.** By N. OTEHA (*Zeit. angw. Chem.*, 1897, 330—331).—A quantity of the finely powdered material varying from 0·1 to 5 grams is boiled in a Wiborgh's apparatus with water, and some pieces of zinc or aluminium foil until all the air is expelled; hydrochloric or sulphuric acid is then introduced, and the boiling is continued for about 20 minutes. By this treatment, the sulphur is converted into hydrogen sulphide, which is carried off by the current of hydrogen; this is passed into a suitable absorbent such as bromine dissolved in hydrochloric acid so as to convert it into sulphuric acid, which is then estimated as usual, or it may be passed through a solution of cadmium acetate and estimated colorimetrically.

L. DE K.

**Estimation of Nitrites and Nitrous Acid.** By BRUNO GRÜTZNER (*Arch. Pharm.*, **235**, 241—245).—Nitrites may be estimated by adding potassium chlorate (free from chloride), excess of decinormal silver nitrate, and nitric acid, to the solution; the nitrous acid liberated decomposes the chloric acid with formation of nitric acid and hydrochloric acid, and the excess of silver is then titrated either with decinormal sodium chloride or decinormal ammonium thiocyanate. The difference between this and the amount of decinormal

silver originally added gives the hydrogen chloride formed, and consequently the nitrous acid originally present. J. F. T.

**A New Reagent for Detecting and Estimating Nitrites.** By M. C. Schuyten (*Chem. Zeit.*, 1896, **20**, 722—723).—Antipyrin, which is so readily detected by means of nitrous acid, is, in turn, a valuable test for nitrites.

A 10 per cent. solution of antipyrin in acetic acid is made, and, when required, is diluted with water to ten times its bulk; 5 c.c. of this reagent is then added to 5 c.c. of the liquid under examination. Even when the amount of nitrous acid does not exceed 1 in 20,000, a permanent green coloration is noticed; the reaction is not interfered with by the presence of the heavy metals or of organic matter, but the colour at once changes to yellow if ferric salts or free hydrochloric or sulphuric acid is present.

The reaction may be utilised for the colorimetric estimation of nitrites in water, particularly as the presence of organic matters does not affect the reaction. A very weak standardised solution of a nitrite is used for comparison. L. de K.

**Estimation of Phosphoric Acid in Organic Substances.** By C. Garola (*Chem. Centr.*, 1896, ii, 597; from *Rev. chim. anal. appliq.*, 1896, 269).—Estimation in the ash always gives low results. The author destroys the organic matter by heating with sulphuric acid as in Kjeldahl's process, neutralises with ammonia, acidifies with nitric acid, and precipitates the boiling solution with molybdate. The weight of the washed precipitate, after drying at 90°, when multiplied by 0·0354, gives the amount of $P_2O_5$. Solutions containing much silica are treated with ferric sulphate and precipitated by ammonia. The precipitate, after drying at 100—110°, is dissolved in nitric acid, the solution filtered from silica, and the phosphoric acid precipitated from the filtrate. M. J. S.

**Estimation of Phosphoric Acid in Medicinal Wines.** By F. Glaser and K. Mühle (*Chem. Zeit.*, 1896, **20**, 723).—One hundred c.c. of the sample is evaporated to a syrupy consistence in a 250 c.c. Kjeldahl flask, 25 c.c. of nitric acid is then added, and a gentle heat applied until an action is set up. When this has ceased, 75 c.c. more of the acid is added and the liquid is evaporated nearly to dryness over a small flame. When cold, 10 c.c. of sulphuric acid is added to the residue, also a drop of mercury, and the whole is boiled until colourless. The liquid is then diluted to the mark with water and 100 c.c. (equivalent to 40 grams of sample) is pipetted off, and after neutralising with ammonia the phosphoric acid is estimated by the citrate, or better still, by the molybdate process. L. de K.

**Detection of Arsenic.** By Dinkler (*Chem. Centr.*, 1896, ii, 851; from *Pharm. Zeit.*, **41**, 638).—The author's method of employing Reinsch's test is to place a piece of clean copper foil in the mixture of the suspected matter with hydrochloric acid, and then to heat for

2 minutes very cautiously, so as to prevent the mixture from becoming brownish. Five minutes later, the foil is removed, dried, and heated in a tube in the usual manner. M. J. S.

**Estimation of Boric Acid.** By A. BELLOCQ (*Chem. Centr.*, 1896, ii, 563; from *Rev. intern. falsific.*, **9**, 119).—The following method, based on the solubility of boric acid in ether (0·8 gram in a litre) has been used in the analysis of the sulphuretted waters of Eaux Chaudes. The desulphuretted water is made alkaline and after being evaporated to dryness, the residue is incinerated, taken up with hydrochloric acid, and the excess of acid completely expelled at a moderate heat; the pulverised residue is then exhausted with ether in a separating bulb, and the ethereal extract evaporated over sulphuric acid in a desiccator. The residue is weighed and regarded as $H_3BO_3$. A qualitative test may be made by passing gaseous ammonia into the ethereal solution, which becomes turbid from formation of ammonium borate. M. J. S.

**Estimation of Boric Acid.** By SCHNEIDER and GAAB (*Chem. Centr.*, 1896, ii, 878; from *Pharm., Centr. H.*, **37**, 672—673).—Boric acid volatilises so readily with absolute alcohol, that a 0·5 per cent. solution leaves scarcely any residue on distillation. To examine flesh for boric acid, the finely divided substance is heated in a covered beaker on the water bath, powdered when cold, and rubbed with anhydrous sodium sulphate to absorb the water; it is then extracted with boiling absolute alcohol, and the filtered extract distilled. The distillate is mixed with soda, evaporated, and the boric acid estimated by known methods. M. J. S.

**Estimation of Boric Acid in Foods.** By LEONARD DE KONINGH (*J. Amer. Chem. Soc.*, 1897, **19**, 55—56).—The process recommended applies to raw yolk of egg and also to milk. The sample, after being rendered alkaline with sodium hydroxide, is incinerated, the ash is boiled with water, and the alkaline filtrate rendered distinctly acid to methyl-orange by means of weak sulphuric acid. After boiling to expel any carbonic anhydride, the liquid is cooled and mixed with half its bulk of glycerol. The boric acid is then titrated with decinormal soda, using phenolphthalein as indicator (Thomson's process). On account of the presence of soluble phosphoric acid, the titration will be somewhat in excess of the truth, but a correction for this may be made by allowing 3 c.c. of soda when operating on 5 grams of yolk of egg, or 1 c.c. when operating on 10 grams of milk. When the acid is present, in large and consequently harmful quantities, the results are sufficiently accurate. L. DE K.

**Estimation of Boric Acid as Potassium Borofluoride.** By KONSTANTIN THADDÉEFF (*Zeit. anal. Chem.*, 1897, **36**, 568—637).—The accurate estimation of boric acid has long been recognised as one of the most difficult analytical operations; Rose and others confined their methods to the estimation of the bases, and calculated the boric acid from the deficiency. The author, being desirous of analysing a specimen of the rare mineral, sulfoborite (a double magnesium borate and sulphate), obtained from the residues of carnallite solutions,

previous analyses, when boric acid was estimated by difference, having shown a deviation of 1·88 per cent. from the theoretical proportion, made a preliminary study of the methods proposed for the estimation of boric acid; these are reviewed at considerable length, and their weak points indicated. By analyses of a specimen of pure crystallised borax, he shows how unsafe it is to trust to a differential method, even in so simple a case. A modification of the Berzelius-Stromeyer method, when performed exactly according to the following description, affords unexceptionable results. Since the method requires the absence of all bases except potassium, it is necessary, when dealing with borates, to employ Rosenbladt's method of distillation with sulphuric acid and methylic alcohol, which, according to Rieschle, is more exact than that proposed by Gooch (Abstr., 1887, 299). Rosenbladt's apparatus is, however, simplified; a flask is fitted with a tube for the admission of purified air, a stopcock thistle funnel with safety bend, and a long delivery tube dipping into a solution of potassium hydroxide in a platinum basin. It is best to mix the sulphuric acid (2—3 c.c.) with 10 c.c. of methylic alcohol in a separate vessel, and introduce it through the funnel after cooling. The air supply, which is controllable by a stopcock, assists greatly in maintaining the regularity of the distillation. For quantities of boric acid ($H_3BO_3$) up to 1 gram, 2 grams of the purest potash (80 per cent. of KHO) in 200 c.c. of water is placed in the basin. After four quantities of methylic alcohol (10 c.c. each) have been distilled over, the contents of the basin are concentrated to one-half on the water bath, an excess of pure hydrofluoric acid is then added, and the evaporation continued until the odour of hydrofluoric acid has almost disappeared. After cooling, 50 c.c. of a clear solution of potassium acetate of 1·14 sp. gr. is added, and the contents of the basin are frequently stirred during 2 hours with a platinum rod, to effect the solution of the potassium hydrogen fluoride; warming at this stage must be avoided. 100 c.c. of alcohol (sp. gr. 0·805) is then added, and after thorough stirring, the whole is left for 12—14 hours. Meanwhile the filter is prepared; a Schleicher and Schull, No. 590, 9 cm. in diameter, is moistened with alcohol (which is found to increase its dry weight by 1—2 miligrams), dried at 100—110° for 2—3 hours, and weighed in a well-fitting stoppered tube. The undissolved residue of potassium borofluoride is transferred from the basin to the filter by rinsing with alcohol of 0·805 sp. gr., with which also it is further washed until a drop of the filtrate leaves no more residue on platinum foil than would be left by an alcoholic solution of the borofluoride (0·000014 gram per c.c.). On account of this solubility, the amount of alcohol should be restricted as much as possible; 60—70 c.c. usually suffices, and the washing is much facilitated by tapping and shaking the funnel; the filter and precipitate are dried for 3 hours as above and weighed. The success of the method depends on the fact that the special mixture of acetate and alcohol is capable of retaining potassium hydrogen fluoride in solution, and that the mixture of the three substances, in the proportions resulting from the use of 2 grams of potash, has an extremely feeble solvent action on the potassium borofluoride. The weighed precipitate should be tested for fluorides by boiling with water and adding calcium chloride to the

cold filtered extract. Out of seven analyses of borax by the above method, only two deviated more than 0·07 per cent. from the theoretical proportion of $B_2O_3$. M. J. S.

**Rapid Method for Estimating Silicon in Silicospiegel and Ferrosilicon.** By C. B. MURRAY and G. P. MAURY (*J. Amer. Chem. Soc.*, 1897, **19**, 138—139).—0·5 gram of the finely divided sample is placed in a dish, 50 c.c. of water, 10 c.c. of hydrochloric acid (sp. gr. 1·2) and 12 c.c. of dilute sulphuric acid (1 : 3) are added and the whole evaporated until copious fumes of sulphuric acid are given off. When cool, 10 c.c. of hydrochloric acid is added and then 70 c.c. of water. On boiling, no effervescence should be noticed; if any occurs, the liquid must again be evaporated until sulphuric acid fumes make their appearance. The undissolved residue is collected, thoroughly washed with dilute hydrochloric acid (1 : 1) and hot water, ignited in a platinum crucible, and weighed. A few drops of sulphuric acid are added to the weighed residue, then enough hydrofluoric acid to dissolve the silica, the whole is evaporated, and the residue ignited to decompose the sulphates; the loss in weight equals the silica, which is then calculated to silicon. It is stated that an analysis may be finished in 30 minutes.

L. DE K.

**Electrolytic Examination of Silicates.** By MAYENÇON (*Chem. Centr.*, 1896, ii, 925; from *Ind. minérale*; *Berg.-Hüttenm. Zeit.*, **55**, 333).—The most insoluble silicates are decomposed by electrolysis if powdered and made into a paste with water, the silicic acid passing to the positive and the other elements to the negative electrode. The silicate paste should be placed on a metal plate connected with the negative pole, and covered with a piece of filter paper upon which the positive plate is laid. If the latter consists of silver, zinc, or copper, silicates of these metals are formed. M. J. S.

**Limits of Delicacy of Various Tests for Metals.** By B. NEUMANN (*Chem. Zeit.*, 1896, **20**, 763—764).—The author has compiled an exhaustive table showing the highest degree of dilution in which a reaction is still visible with the tests for the more important metals. The names of the various observers are given, the author himself being responsible for 62 of the statements. L. DE K.

**Estimation of Alkalis in Fire-Clays.** By CARL REINHARDT (*Chem. Centr.*, 1896, ii, 265—266; from *Stahl. ü. Eisen.*, **16**, 448—452).—After the sample has been treated with hydrofluoric and sulphuric acids to remove the silica, the residue is dissolved in boiling water, and the solution made alkaline with ammonia, using rosolic acid as indicator; hydrogen peroxide is then added to complete the precipitation of the alumina, oxide of iron, &c. After making up to a definite bulk, two-thirds of the liquid is filtered, evaporated to dryness, and carefully ignited; the residue is then again treated with a few drops of the acid mixture, and, after ignition, boiled with a little hydrochloric acid. After diluting with water, the lime is precipitated by ammonia and ammonium oxalate, the filtrate evaporated to dryness, and the residue ignited to expel the ammoniacal salts. The residue is then taken up with water, and the clear solution mixed with excess of sulphuric

acid; this, on evaporation, leaves the magnesia, potash, and soda as sulphates. After strongly heating with addition of some solid ammonium carbonate, the mixed sulphates are weighed, and then dissolved in a measured quantity of water. In one half of the liquid the magnesia is estimated, in the other half the sulphuric anhydride, the alkalis thus being obtained by difference.

The author advises making a blank experiment, so as to allow for any traces of alkalis in the reagents. L. DE K.

**Direct Estimation of Calcium Carbonate in Soil.** By FAUSTO SESTINI (*Ann. Agron.*, 1897, **23**, 326—327).—The soil (5 grams) is boiled for an hour with 1 per cent. acetic acid (100 c.c.) in a reflux apparatus, allowed to cool, and filtered through a dry filter paper; 55 c.c. of the filtrate is evaporated to 5 c.c., treated with hydrochloric acid (sp. gr. = 1·1), and evaporated until all the acetic acid has disappeared. The residue is then dissolved in a little water, and ammoniacal solution of ammonium chloride (10 c.c.) added, after which the volume of the liquid is made up to 55 c.c. with 75 per cent. alcohol. The precipitate (calcium sulphate and ferric oxide) is separated by filtration, and 50 c.c. of the filtrate (corresponding with 2·5 grams of soil) precipitated with ammonium oxalate. N. H. J. M.

**Estimation of Zinc by Electrolysis.** By EDUARD JORDIS (*Chem. Centr.*, 1896, ii, 449—450; from *Zeit. Elektrotech. ü. Elektrochem.*, **2**, 655—657).—Platinum dishes may be quickly coated with copper by using a cold saturated solution of copper sulphate mixed with 5 per cent. of nitric acid; at a temperature of 50—60° and with a current of 1—1·5 ampère, the operation is finished in 2 minutes. The zinc solution, measuring from 120—150 c.c. and containing from 0·3—0·5 gram of metal, is mixed with 2 grams of ammonium sulphate, 5—7 grams of ammonium lactate, and a few drops of lactic acid, and introduced into a copper-coated platinum dish. To prevent the oxidation of the zinc, the dishes should not be filled too full, so as to leave a few mm. of copper deposit above the surface of the liquid. When, after 40 minutes, the bulk of the metal has been deposited, using a current of 1—1·5 ampère, the liquid is poured into a second platinum dish and the electrolysis continued for another 20—25 minutes.

When a speedy result is desired, the electrolysis may be conducted at the boiling temperature; in this case, the liquid must be kept from getting too acid by cautiously adding ammonia. L. DE K.

**Contributions to Qualitative Analysis.** By ALVAREZ and JEAN (*Chem. Centr.*, 1896, ii, 513—514; from *Répert. Pharm.*, 1895, 440).—*Detection of Zinc, Chromium, Manganese, and Iron.*—The solution is boiled with excess of aqueous potash, filtered, and the filtrate tested for zinc by means of sodium sulphide. The potash precipitate is then boiled with aqueous potash and excess of lead dioxide; if chromium is present, a yellow solution is obtained from which lead chromate is thrown down on adding acetic acid. The undissolved lead dioxide, when boiled with nitric acid, gives a violet coloured solution if manganese is present. The iron is then tested for by pouring off the nitric acid, dissolving the residue in hydrochloric acid, and adding potassium thiocyanate.

*Detection of Alkali Sulphides, Thiosulphates, and Sulphites.*—Sulphides are tested for by sodium nitroprusside, which gives a violet coloration. A portion of the solution is mixed with an ammoniacal solution of zinc oxide, heated to expel the ammonia, filtered, and the filtrate tested for sulphite and thiosulphate by adding, first 6 times its bulk of 95 per cent. alcohol, and then, cautiously, a solution of bismuth subnitrate in nitric acid. The presence of thiosulphate is indicated by a dense, yellowish-brown precipitate of bismuth thiosulphate; this is allowed to subside, and then more of the reagent is added, when a white precipitate is formed if a sulphite is present. The presence of a sulphite may also be detected by means of iodic acid, starch solution, and acetic acid.

*Detection of Chlorides, Chlorates, and Nitrates.*—After removing the whole of the chloride by silver acetate, acetic acid and zinc are added to the filtrate and the whole is warmed; a further precipitate of silver chloride is first formed if a chlorate is present, but this is gradually reduced to metallic silver. The zinc and acetic acid convert the nitric acid into ammonia, which may be detected by means of Nessler's reagent. L. DE K.

**Estimation of Mercuric Salts.** By LUDWIG VANINO and F. TREUBERT (*Ber.*, 1897, **30**, 1999—2001).—To the solution of mercuric salt (containing about 0·5 gram Hg per 100 c.c.), hydrogen peroxide is first added, and then, gradually, commercial hypophosphorous acid (of sp. gr. 1·15) in slight excess; the precipitate of mercurous chloride is washed with cold water, collected on a tared filter, dried at 100°, and weighed. The presence of hydrogen peroxide prevents a further reduction of the mercurous chloride to mercury, which otherwise takes place. In 8 experiments with mercuric chloride, the percentage of Hg as found varied from 73·80 to 73·99, the calculated percentage being 73·80. C. F. B.

**Improvements in the Colorimetric Test for Copper.** By GEORGE L. HEATH (*J. Amer. Chem. Soc.*, 1897, **19**, 24—31).—The following process is recommended. 2·5 grams of the material, lean blast-furnace slags, for example, is heated in a porcelain dish with 15 c.c. of nitric acid, and after adding 5 c.c. of sulphuric acid the evaporation is continued until the mass has become a thick, but rather soft, paste; it is then treated with 70 c.c. of water to dissolve the copper sulphate, and 30 c.c. of ammonia is added. The liquid is filtered, and the residue after being twice washed with 10 c.c. of dilute ammonia (1 : 10), is rinsed back into the dish, using 50 c.c. of water, taking care not to damage the filter, and enough sulphuric acid is added to redissolve the iron and alumina; 25 c.c. of ammonia is again added, and the filtrate and ammoniacal washings are mixed with the main filtrate, which is then transferred to a tall cylinder of thin, colourless glass, and made up with dilute ammonia to 200 c.c. The colour of the liquid is compared with those of a series of copper solutions of known strength contained in similar cylinders; these standard solutions keep very well if the copper is present as sulphate and the liquid contains a large excess of ammonia, provided they are kept from the light in a cool place. L. DE K.

**Estimation of Copper in Vegetable Foods.** By VICTOR VEDRÖDI (*Chem. Zeit.*, 1896, **20**, 584—585).—The author recommends eliminating any soluble silicic acid and also the oxide of iron from the ash of vegetable foods when testing the same for copper. If this precaution be not taken, the precipitate which always forms on adding ammonia to the acid solution of the ash will carry down with it a not inconsiderable amount of copper, and the filtrate will be deficient in colour.

Instead of burning the sample, it may also be "mineralised" by heating first with nitric acid and then with strong sulphuric acid.

L. DE K.

**Analysis of Aluminium and its Alloys.** By HENRI MOISSAN (*Compt. rend.*, 1897, **125**, 276—278).—The residue left when aluminium is treated with dilute hydrochloric acid (20 : 100) contains at least 10 per cent. of iron, and does not consist only of carbon, copper and silicon, as Balland has stated (*Compt. rend.*, **124**, 1311); on the other hand some of the copper is dissolved even when a more dilute acid (10 : 100) is used. Further, when the aluminium is treated with hydrochloric acid (10 : 100) to which a small quantity of nitric acid is added, the residue does not consist of carbon and silicon only, as Balland stated, but contains a large proportion of iron and about 10 per cent. of copper.

Some recent specimens of aluminium were found to contain 99·21 to 99·61 per cent. of that metal, with 0·41—0·54 per cent. of iron, 0·05—0·11 of silicon, 0·00—0·02 of sodium, and traces of copper.

C. H. B.

**Detection of Alum in Flour and Bread.** By JOSEF VAN DER PLANCKEN (*Chem. Centr.*, 1896, ii, 563; from *Ann. Pharm. Louvain*, 1896, May).—The test with campeachy wood tincture succeeds only with fresh flour, and fails with sour bread. From 10 to 20 grams of flour or powdered bread is made into a paste with water, some sodium chloride (free from carbonate) is added, then 10 drops of fresh logwood tincture and 5 grams of calcium carbonate, and the whole is made up to 100 c.c. The clear, supernatant liquid will exhibit a bluish-grey coloration in presence of 0·1 per cent. of alum; in the absence of alum, the liquid is reddish-violet.

M. J. S.

**Estimation of Calcium, Aluminium, and Iron in Mineral Phosphates.** By LÉON LINDET (*Compt. rend.*, 1897, **125**, 246—247).—In the ordinary method for the analysis of mineral phosphates, the phosphoric acid is precipitated by magnesia mixture in presence of a large quantity of ammonium citrate, and the destruction of this salt for the purpose of estimating iron, &c., is troublesome and tedious. Citric acid and citrates can, however, readily be oxidised by means of the reaction described by Villiers (this vol., ii, 492). The solution is acidified with nitric acid, 0·5 gram of manganese sulphate or nitrate added, and then 50 c.c. of concentrated nitric acid for every 20 grams of citric acid present; the liquid is carefully heated, and more nitric acid is added from time to time until there is no further evolution of gas. The metals are afterwards separated in the usual way.

Vanadyl dichloride acts much more energetically than manganese salts, and 0·1 gram will readily bring about the oxidation of 20 grams of citric acid. As ammonium hypovanadate is insoluble in excess of ammonia, it is precipitated with the ferric and aluminium hydroxides, and the weight of the vanadium oxide must be subtracted from the weight of the mixed oxides which are left after strongly heating. It is convenient to use a 1 per cent. solution of vanadyl dichloride, the strength of which is checked by precipitating 10 c.c. of the solution with ammonia in presence of a known quantity of a ferric salt, and weighing the precipitate after strongly heating.

In either case, the calcium is estimated in the usual way in the liquid from which aluminium, iron, and manganese or vanadium have been removed. C. H. B.

**Detection of Nickel in Presence of Cobalt.** By Anselmo Cavalli (*Gazzetta*, 1897, **27**, ii, 95—96).—In the group precipitate, the author extracts the zinc and manganese sulphides from those of cobalt and nickel by dilute hydrochloric acid (1 : 5) and after washing the residue with very dilute ammonium sulphide, dissolves it in nitro-hydrochloric acid, evaporates to dryness, and adds a little water; on treating the solution with sodium nitroprusside, both nickel and cobalt are precipitated, although only slowly from dilute solutions. The nickel compound is dissolved on treating this precipitate with dilute ammonia, but not the cobalt. W. J. P.

**Complete Analysis of Iron Ores: Notes on Särnström's Method of Estimating Manganese.** By George Auchy (*J. Amer. Chem. Soc.*, 1897, **19**, 139—153).—When using Särnström's process for estimating manganese in presence of iron, it is necessary to be very careful not to add any excess of sodium carbonate before titrating with potassium permanganate, as otherwise the precipitated ferric oxide may carry down a small proportion of the manganese; the author states that this danger is greatly lessened if about 7 grams of ammonium chloride is added before the soda.

A process for the full analysis of iron ores is given, of which the following is an outline. The ore is dissolved in hydrochloric acid, the siliceous matter separated by evaporation, the residue treated with acid, and the filtrate largely diluted. After adding a sufficiency of ammonium chloride, the excess of acid is first neutralised with solid sodium carbonate, and then a solution of the latter is added until a precipitate begins to form; on boiling, the bulk of the iron is precipitated, and the last traces are thrown down on adding a few more drops of soda solution. The filtrate, after being heated to boiling, is mixed with ammonia to precipitate the alumina, filtered, and the manganese in the filtrate titrated with permanganate. The liquid, which may contain calcium and magnesium, after removal of all the manganese as sulphide, may be analysed in the usual manner.

The alumina precipitate is dissolved in hydrochloric acid; the ferric precipitate also and the two solutions are united; the iron and aluminium are now precipitated by ammonia, and the filtrate, which may contain calcium and magnesium, may be advantageously united with the main calcium and magnesium solution. The oxides of iron and

aluminium, after having been weighed together, are dissolved, and the iron is estimated volumetrically. L. DE K.

**Estimation of Tin in Tin Plate.** By HUGO MASTBAUM (*Zeit. angw. Chem.*, 1897, 329—330).—Twenty-five grams of the material, cut up into small pieces, is boiled with 50 c.c. of hydrochloric acid containing 10 per cent. of HCl. The tin coating soon dissolves, and the solution is at once poured off and diluted to 250 c.c.; 50 c.c. of it is then introduced into a 100 c.c. flask, neutralised with ammonia, and mixed with 10 c.c. of yellow ammonium sulphide. Water is now added up to the mark, the mixture filtered, and 50 c.c. is pipetted off and acidified with acetic acid to precipitate the stannic sulphide.

When completely settled, the precipitate is collected on a filter and washed with a 10 per cent. solution of ammonium acetate. The sulphide is converted into stannic oxide in the usual manner by roasting and final ignition with addition of a lump of ammonium carbonate.

L. DE K.

**Action of Hydrogen Peroxide on Metals as Precipitated by Hypophosphorous Acid: Detection of Arsenic, Antimony, and Bismuth in the Presence of the Noble Metals.** By LUDWIG VANINO (*Ber.*, 1897, **30**, 2001—2003).—The metals are precipitated by warming the acid solution with hypophosphorous acid; gold, silver, and mercury are even precipitated in the cold (platinum, iridium, and rhodium are not precipitated at all). The arsenic, antimony, and bismuth (also copper) in this precipitate can be dissolved by means of hydrogen peroxide, and their presence demonstrated by warming the solution with hypophosphorous acid; gold, silver, mercury, ruthenium, palladium, and osmium are not dissolved. C. F. B.

**Apparatus for Testing Oils.** By A. GAWALOWSKI and ALEXANDER KATZ (*Chem. Centr.*, 1896, ii, 451; from *Centr. Nahr. ü. Genussm. ü. Hyg.*, **2**, 213—214).—When testing fatty or mineral oils, or a mixture of the same, it is advisable to determine the coefficient of solubility in alcohol and ether as proposed by Gawalowski. For this purpose, 2·5 grams of the sample is dissolved in 10 c.c. of ether slightly coloured with "alkannin 1," 4 c.c. of this solution is placed in a specially constructed apparatus, and 95 per cent. alcohol is gradually added from the burette which forms part of the apparatus, until the liquid turns red and turbid, so that the printed lines of the paper on which the apparatus is placed are no longer visible. Suppose 10·2 c.c. of alcohol are required, the degree of coefficient of solubility will be 10·2. Different samples of oil give very different figures.

The apparatus is so constructed that no perceptible evaporation of ether can take place during the titration. L. DE K.

**Analysis of Essence of Lemons.** By ARTURO SOLDAINI and E. BERTÉ (*Gazzetta*, 1897, **27**, ii, 25—34).—The authors' method for detecting the adulteration of lemon oil (*Sull' analisi dell' essenza di limone*, Messina, 1896) having been recently criticised (*Schimmel's Report*, April, 1897, 19), the authors quote more analytical data, and state that adulteration can always be detected by their method, although the quantity of foreign oil added may not be always ascertainable.

Although citral cannot be accurately determined in lemon oil, yet, if it could, the determination would hardly help in detecting adulteration, the proportion of citral in genuine lemon oil being very variable.

Lemon oil is genuine if, after distilling off one-half of the sample, the distillate has a higher rotation than, and the residue a rotation lower than, or equal to, that of the original oil; the difference must be at least 0° 30′. If 2 per cent. of turpentine is added, this difference disappears, and the addition of a larger quantity causes the difference to be of opposite sign. W. J. P.

**Analysis of Coals.** By FRITZ HABER and S. GRINBERG (*Zeit. anal. Chem.*, 1897, **36**, 557—567).—The valuation of the calorific power of a coal by estimating the carbon and hydrogen has hitherto presented difficulties, due mainly to the fact that methane is burnt by copper oxide only at a temperature high enough to soften combustion tubing. The authors obviate this difficulty by the use of platinised asbestos, which effects the combustion of methane in oxygen at 414°. The combustion tube, 430 mm. in length, is charged as follows: 30 mm. are left empty; then comes a plug of copper gauze 10 mm. in length; after this 60 mm. of granular lead chromate, a 5 mm. plug of copper gauze, next 1 gram of 10—20 per cent. platinised asbestos teased out so as to occupy 100 mm. of the tube, and finally a gauze plug 5 mm. long. The remainder is left empty to receive the boat containing the coal, and so much of the tube as is occupied by the above materials, as well as a sufficient length to include the boat, but not the whole tube, is wrapped in stout copper gauze. To the empty end of the tube is attached the usual absorbing apparatus, whilst to the other is fitted a T-piece, through the horizontal limb of which a wire (stout copper with a platinum end) can be worked backwards and forwards in its caoutchouc stopper. The platinum wire is hooked, and serves either to push the boat forward or pull it back. The tube is heated by two Teclu burners. The boat, containing about 0·25 gram of coal, is placed in the uncovered part of the tube, purified oxygen is admitted by the side limb of the T-piece at the rate of 2—3 bubbles per second, and the boat is then slowly pushed forward (about 10 mm. every 10 minutes) into the heated region until it touches the copper plug. In this way, any moisture it contains is first driven off, and the expulsion of the volatile hydrocarbons then takes place gradually. The coke should burn with a red glow; if it glows with a yellow light, the oxygen stream and the whole combustion are too rapid. A single tube suffices for 8—10 analyses, and excellent results are obtained with coals of widely varying composition. No provision being made for the reduction of nitrogen oxides, traces of nitrous and nitric acids are found in the absorbing apparatus, but their amount is too small to be of technical importance; it is stated that sulphuric acid is not found.

M. J. S.

**Estimation of Alcohol in Essences.** By RUDOLF HEFELMANN (*Chem. Centr.*, 1896, ii, 932—933; from *Pharm. Centr.-H.*, **37**, 683).—The official method consists in diluting with about 2 volumes of water and mechanically precipitating the ethers by addition of solid sodium chloride, then distilling out the alcohol from the sodium chloride

solution. The method does not give satisfactory results with eau de Cologne. From essences diluted until the alcohol amounts to 40—60 grams per 100 c.c., the ethers and aromatic oils can be removed by shaking with light petroleum (sp. gr. = 0·64—0·67; boiling point 55—75°); 25 c.c. of essence is therefore diluted with an appropriate volume of water, shaken in a separator bulb with 50 c.c. of light petroleum, and after 3—5 hours' repose the clear lower layer is run off, and a measured volume of it, further diluted with half its volume of water, is distilled. The alcohol in the distillate is ascertained by taking the specific gravity in the usual manner. All the liquids should be at 15° when measured. M. J. S.

**New Reaction of Picric Acid.** By A. Swoboda (*Chem. Centr.* 1896, ii, 717; from *Z. Oesterr. Apoth.-V.*, **34**, 617).—On treating a cold aqueous solution of picric acid with a cold aqueous solution of methylene-blue, there is immediately produced a violet, flocculent precipitate, soluble with blue or green colour in ether, chloroform, or hot water. The chloroform solution leaves a blue residue when evaporated. Lacquers coloured with picric acid are first dissolved with a little alcohol. M. J. S.

**Improvements in Paper Testing.** By Siegmund Ferenczi (*Zeit. angw. Chem.*, 1897, 436—441).—The sample is examined microscopically; this investigation being much assisted by using appropriate staining materials such as a solution of malachite-green acidified with acetic acid, or a weak alcoholic solution of rosaniline sulphate containing excess of sulphuric acid. If excess of incrustating matter such as lignin or lignose is found, the paper cannot be considered as likely to be very durable.

In order to test the capacity of a sample of paper to resist crumpling, the author prefers using either the apparatus devised by Pfuhl or the one invented by Schopper. For details of these complicated pieces of apparatus, the original paper should be consulted. L. de K.

**New Method of Detecting Formaldehyde.** By Lebbin (*Chem. Centr.*, 1896, ii, 930; from *Pharm. Zeit.*, **41**, 681).—A few c.c. of a formaldehyde solution mixed with about 0·05 gram of resorcinol, and then with about its own volume of 50 per cent. soda solution, when boiled, develops a rich, permanent red coloration. The reaction is not given by other aldehydes. It will detect 1 part of formaldehyde in 10 million of water. M. J. S.

**Estimation of Aldehyde in Alcoholic Liquids.** By E. Rieter (*Chem. Centr.*, 1896, ii, 368; from *Schweitz. Wochs. Pharm.*, **34**, 237—239).—When dealing with a colourless liquid, 5 c.c. of 0·05 per cent. sulphurous acid is put into a 100 c.c. flask together with 20 c.c. of the liquid to be tested, which should not contain more than 0·0025 per cent. of aldehyde; after making up to the mark with water and thoroughly mixing, it is put aside for 4 hours. Fifty c.c. of the mixture is taken out, and the free sulphurous acid is titrated, as usual, with N/200, or, if more aldehyde was present and consequently more sulphurous acid entered into combination, with N/100 iodine. The remainder of the liquid is mixed with 25 c.c. of normal potash

which rapidly decomposes the compound and the total sulphurous acid is then titrated as before, after adding a sufficiency of dilute sulphuric acid. The difference between the two titrations represents the amount of sulphurous acid combined with the aldehyde.

Coloured alcoholic liquors are first diluted with water and then submitted to distillation, the colourless distillate being treated as described above. L. DE K.

**Estimation of Hydrocyanic Acid in Oil of Bitter Almonds.** By EDWARD KREMERS and O. S. SCHREINER (*Chem. Centr.*, 1896, ii, 928; from *Pharm. Review*, 1896, Sept.).—Silver nitrate is added to an aqueous solution of the oil, then excess of ammonia, and immediately afterwards nitric acid. The object of the ammonia is to decompose the benzalcyanhydrin, in which most of the cyanogen of the oil is contained, and from which it cannot be directly precipitated by silver nitrate. The hydrocyanic acid may be titrated with silver nitrate (using chromate as indicator) if the oil is mixed with a paste of magnesium hydroxide. M. J. S.

**Estimation of Volatile Fatty Acids by the Leffmann-Beam Process.** By W. KARSCH (*Chem. Zeit.*, 1896, 20, 607—608).—The author recommends this process for the analysis of butter, as it dispenses with the use of alcohol and so prevents the results being vitiated by the absorption of carbonic anhydride during the evaporation.

This process, as will be remembered, consists in saponifying the butter with a solution of sodium hydroxide in glycerol. L. DE K.

**Detection of Lactic Acid and its Clinical Significance.** By J. H. DE JONG (*Chem. Centr.*, 1896, ii, 806—807; from *Arch. f. Verdauungskrankh.*, 2, Part I.).—To detect free lactic acid in the gastric juice by Uffelmann's test, 5 c.c. of the gastric juice mixed with 1—2 drops of hydrochloric acid is cautiously evaporated to a syrupy consistence and extracted with a little ether. The ethereal solution is added drop by drop to 5 c.c. of boiling water in a test-tube, and when the ether has evaporated and the water cooled, a drop of a 5 per cent. solution of ferric chloride is added. The colour is then compared with that produced in a standard solution of lactic acid. For clinical purposes, Nessler's test is too sensitive; Boas' method (*Chem. Centr.*, 1894, i, 338; ii, 334) is more suitable. Regard should be paid to the combined as well as the free lactic acid. The ethereal extract obtained from 20 c.c. of gastric juice by Boas' process is heated in a flask with manganese dioxide and sulphuric acid, and the aldehyde produced is collected in a bottle connected air tight with the Liebig's condenser, charged with 20 c.c. of water and plunged in ice. The stopper of the bottle is furnished with a second tube, which also passes through the condenser jacket and serves for the escape of air without loss of aldehyde. After distilling over three-quarters of the solution and aspirating air through the apparatus, an excess (20 c.c.) of N/10 iodine solution and 20 c.c. of pure soda are added, and after a few minutes the clear liquid is acidified and the amount of iodine not consumed in forming iodoform is titrated by thiosulphate. Healthy gastric juice contains

only traces of lactic acid. Larger amounts may be formed in cases where secretion and peristaltic action are both deficient, but in the absence of gastric carcinoma its formation is exceptional; in the presence of carcinoma, it occurs almost invariably. M. J. S.

**Detection of Calcium Hydrogen Tartrate in Purified Cream of Tartar.** By HENRIK ENELL (*Chem. Centr.*, 1896, ii, 515; from *Nordisk. Farm. Tidskr.*, **11**, 393).—One gram of the sample is charred, the residue extracted with very dilute hydrochloric acid, and the filtered solution mixed with excess of ammonia and ammonium oxalate; the precipitated calcium oxalate is then treated in the well-known way with standard potassium permanganate. L. DE K.

**Estimation of Uric Acid in Guano.** By ALBERT STUTZER and A. KARLOWA (*Chem. Zeit.*, 1896, **20**, 721—722).—About two grams of the sample is treated with water feebly acidified with hydrochloric acid, the whole evaporated to dryness, and the residue taken up with 100 c.c. of water in which 3 grams of piperazine has been dissolved; the mixture is then boiled for 1 minute, filtered, coloured with a drop of phenolphthalein solution, and after sufficient hydrochloric acid has been added to destroy the alkaline reaction, 10 c.c. more of 10 per cent. hydrochloric acid is added; the whole is then well stirred and left for 12 hours. The crystallised uric acid which separates is collected on a very small filter, washed with water containing 1 per cent. of hydrochloric acid until the total filtrate measures 200 c.c., after which the filter and its contents are treated by the Kjeldahl process. The amount of nitrogen found, multiplied by 3, gives the uric acid originally present in the guano. As, however, uric acid is not absolutely insoluble in water, a slight correction must be made; the authors advise adding 0·003 gram to the quantity of uric acid found. L. DE K.

**Estimation of Salicylic Acid.** By FRANZ FREYER (*Chem. Zeit.*, 1896, **20**, 820—821).—The author states that salicylic acid may be estimated in the same way as phenol by means of bromine. The solution is treated with a mixture of potassium bromate and potassium bromide; dilute hydrochloric acid is added, and then after about 4 minutes, excess of potassium iodide solution. The liberated iodine is titrated by means of approximately N/10 sodium thiosulphate, a blank experiment being, of course, made, and the difference in the amount of thiosulphate noted. The process cannot be used for estimating this acid in beer or wine, unless the acid has been previously isolated by the use of ether and light petroleum. To test qualitatively for the acid, the author recommends distilling the beer or wine, when the acid will be found chiefly in the last fractions of the distillate; the ferric chloride test may then be applied. Hoorn's statement that beer when distilled yields a substance giving a violet coloration with ferric chloride has not been confirmed by the author. L. DE K.

**Estimation of Kynurenic Acid.** By ACHILLE CAPALDI (*Zeit. physiol. Chem.*, 1897, **23**, 92—98).—Although the methods described by Schmiedeberg and Schultzen (*Annalen*, 1872, **164**, 155) and by

Jaffé for the estimation of kynurenic acid in urine give fairly satisfactory results, they are to be objected to on account of the time which they take, and also because the kynurenic acid obtained is always mixed with colouring matter, which cannot easily be got rid of without loss of material.

The author suggests the following method by which the kynurenic acid is obtained perfectly pure.

The urine is mixed with half its bulk of a 10 per cent. solution of barium chloride containing 5 per cent. of concentrated ammonium hydroxide, evaporated to one-third of the volume of urine taken and acidified with concentrated hydrochloric acid. The precipitated kynurenic acid is filtered, dissolved in aqueous ammonia, reprecipitated, and weighed. A. W. C.

**The Critical Temperature of Liquids and a New Method for Identifying Fats and Oils.** By ALEXANDER VON ASBÓTH (*Chem. Zeit.*, 1896, **20**, 685—686).—The author confirms the results obtained by Crismer, who found that there is a great difference between the critical temperature of butter and margarine. The investigation will be continued. (Compare Abstr., 1896, ii, 506.) L. DE K.

**Use of the Iodine Number in the Analysis of Wool Fat.** By W. HERZIG (*Chem. Centr.*, 1896, ii, 936; from *Ding. Poly. Journ.*, **302**, 17).—The author has already shown that the iodine number can be employed in forming an opinion on a wool fat. He has now examined the iodine absorption of the various groups into which a specimen of wool fat can be separated, with the object of ascertaining the amount of the unsaturated substances in each group, and of employing the iodine absorption of the separated groups as an analytical method. The conclusions arrived at from the examination of a single sample, obtained from a South American wool, by extraction with ether, are as follows. Besides fatty acids, only unsaturated substances exhibiting the same iodine number as cholesterol are present; the presence of isocholesterol is also very probable. Saturated higher alcohols cannot be present, since those in wool fat are readily soluble in organic menstrua, whilst cerylic alcohol is sparingly soluble, and the absence of any considerable amount of such substances is further indicated by the iodine number. The results show that where saponification under pressure is necessary, that operation can be resorted to without more intimate decomposition. After removal of the free fatty acids, the fatty acids obtained by saponification show a very low iodine absorption, and therefore contain a very small proportion of unsaturated fatty acids. Should this condition be found to persist in other specimens, the iodine numbers of these members would afford valuable analytical information. M. J. S.

**Assay of Linseed Oil.** By HUGO AMSEL (*Zeit. angw. Chem.*, 1897, 369—370).—A controversy with Lippert (this vol., ii, 529). Among other things, the author states that an abnormal solubility of the sample in alcohol, or an increased acidity number, does not necessarily point to an admixture of rosin. L. DE K.

**Cause of the Low Iodine Number of Linseed-cake Oil.** By G. FASSBENDER and J. KERN (*Zeit. angw. Chem.*, 1897, 331—332).—By means of cold pressure, it is possible to obtain a commercially pure linseed oil from adulterated seed, as the cake retains the greater part of the foreign oils; the amount of foreign *Cruciferæ* in the original material cannot, therefore, be calculated from the iodine number given by the fat extracted from the cake by solvents. L. DE K.

**Detection of Vanillin in Resins.** By KARL DIETERICH (*Chem. Centr.*, 1896, ii, 364—365; from *Pharm. Centr. Halle*, 37, 424—427). —To detect vanillin in balsam of Peru, gum benzoin, or storax, the author uses a mixture of equal parts of hydrochloric acid and water, which, on warming, readily takes up the vanillin without dissolving any of the resinous matter; after filtering the hot solution through (animal?) charcoal, the pale yellow liquid is tested with pyrogallol or phloroglucinol. The presence of benzoic or cinnamic acids does not interfere with the test.

To estimate the quantity of vanillin, the hydrochloric extract from 1 kilogram of storax is made strongly alkaline, mixed with 20 grams of hydroxylamine hydrochloride, and heated on the water bath for some hours; the vanillin-oxime thus formed is dissolved by agitating the liquid with ether, the latter is evaporated, the residue treated with boiling water, and the solution put aside to crystallise. It seems to be impossible to completely free the compound from cinnamic acid. The vanillin can be readily calculated from the amount of the oxime.

The author has also worked out and used with some success a colorimetric process depending on the pyrogallol reaction, using solutions of pure vanillin of different strengths for comparison. L. DE K.

**New Reagent for Alkaloids.** By ADAM JAWOROWSKI (*Chem. Centr.*, 1896, ii, 321—322; from *Pharm. Zeit. Russ.*, 35, 326—328).— This reagent is prepared by dissolving 0·3 gram of sodium vanadate in 10 c.c. of hot water; when cold, a solution of 0·3 gram of crystallised copper sulphate is added, and then about 8 drops of glacial acetic acid to clear the liquid, which is filtered. The salt of the alkaloid is dissolved in 4—5 c.c. of water if necessary, using a little dilute acetic acid (1 : 18) if it is the free base, and warming gently. One drop of the reagent is added to the solution, and if no precipitate is formed after the lapse of 15 minutes, the mixture is divided into two parts, to one of which a few more drops of the reagent are added, whilst the second portion is heated to boiling; if the liquid becomes turbid in either case, an alkaloid is present.

The following alkaloids are precipitated from solutions containing from 0·01—0·002 per cent.: thebaine, berberine, nicotine, aconitine, strychnine, quinine, quinidine, cinchonidine, cinchonine, brucine, emetine, and apomorphine. On adding excess of acetic acid, the turbidity readily disappears in the case of aconitine, quinine, nicotine, and thebaine; somewhat more slowly in the case of apomorphine (which turns dark blue), berberine, brucine, emetine, and strychnine. The following alkaloids are precipitated from solutions containing at least 0·2 per cent.; morphine, sparteine, papaverine, atropine, narcotine,

and codeine, which appear after 10—60 seconds; also cocaine and hyoscyamine, which only give an opalescence.

The following are not precipitated unless from concentrated solutions: caffeine, colchicine, coniine, cotoine, narceine, pilocarpine, piperine, solanine, theobromine, and veratrine (compare Abstr., 1896, ii, 629). L. DE K.

**Estimation of Caffeine in Tea and Coffee.** By ALBERT HILGER and A. JUCKENACK (*J. Pharm.*, 1897, [vi], **6**, 184—186 and 190—192; from *Apoth. Zeit.*, 1897, **12**, 145 and 422).—Twenty grams of finely ground coffee or powdered tea is digested at the ordinary temperature with 900 c.c. of water for several hours and then boiled, care being taken to replace the water lost by evaporation. Three hours' boiling is necessary for green coffee, only $1\frac{1}{2}$ hours for roasted coffee or tea. After cooling to 60 to 80°, 7·5—8·0 grams of aluminium acetate in solution (basic aluminium acetate solution of the German pharmacopœia) is run in, and then 1·9 grams of sodium hydrogen carbonate is gradually added while the mixture is well stirred; it is then boiled for 5 minutes, allowed to cool, water added to make the total weight 1020 grams, and filtered. 750 grams of the filtrate—corresponding with 15 grams of coffee or tea—to which 10 grams of dried and finely powdered aluminium hydroxide and a little filter paper have been added, are evaporated to dryness, and the residue dried and extracted for 8 hours with purified carbon tetrachloride. The product obtained after removal of the carbon tetrachloride and drying, is practically pure caffeine, containing at most 2—4 milligrams of impurities. Calcium hydroxide cannot be used in estimating caffeine, as it decomposes part of the alkaloid, according to Schultzen's equation, and converts the rest into caffeidine. Lead hydroxide, obtained by means of ammonia, has no action on caffeine, neither has magnesia.

Caffeine obtained by Trillich and Göckel's method from roasted coffee contains large quantities of impurities, whereas that obtained from green coffee is practically pure. The authors think that the second alkaloid of coffee described by Forster and Riechelmann is a pyridine or a similar base produced during the roasting, since it does not occur in green coffee. J. J. S.

**Estimation of Xanthine Bases in Urine.** By ROBERT ARNSTEIN (*Zeit. physiol. Chem.*, 1897, **23**, 417—430).—The methods at present principally used (Haycraft's and Camerer's) for the estimation of uric acid and xanthine bases are compared, and the causes of difference discussed. Some modifications are suggested, but an absolutely trustworthy method appears still to be wanting. W. D. H.

**Detection of Horse Flesh.** By COURLAY and COREMONS (*Chem. Centr.*, 1896, ii, 66—67; from *Ann. de médic. vétérin.*, **10**, 173).—Fifty grams of the fresh and finely divided material is boiled for $\frac{1}{4}$—$\frac{1}{2}$ hour with 200 c.c. of water, the extract filtered through a wetted filter, and a portion of the filtrate treated with a few drops of a solution of 2 parts of iodine, 4 of potassium iodide, and 100 of water. The production of a brown coloration, which disappears at 80° but returns on cooling, indicates the presence of glycogen, and hence of

horse flesh. If the glycogen reaction is masked by the presence of starch, a portion of the filtrate is precipitated with 2—3 volumes of strong acetic acid, and the iodine test applied after filtering. This reaction will distinguish horse flesh from that of oxen, calves, pigs, dogs, and cats, but not from fœtal flesh. The flesh of the masticatory muscles of the horse does not, however, give the glycogen reaction.

M. J. S.

**Method for the Examination of Biliary Calculi.** By GEORGES DENIGÈS (*J. Pharm.*, 1897, [vi], 6, 71—72).—A few grains of the powdered calculus is boiled for half a minute or longer with 2 c.c. of glacial acetic acid. Cholesterol may be tested for by placing a drop of the hot solution on an object glass, allowing the acetic acid to evaporate spontaneously for a few minutes, and then examining under the microscope. The drop is then completely evaporated at a gentle heat, immediately wetted with a drop of alcohol, which is likewise allowed to evaporate, and the crystals (rhombohedral plates), after being moistened with water, are examined under the microscope. If the amount of cholesterol present is large, the acetic acid solution, on cooling, will deposit slender, crystalline needles. The presence of cholesterol may be confirmed by Salkowski's colour reaction. Biliary pigments are often detected by the green colour of the acetic acid solution; if this solution is not green, then a small quantity is added to a drop of a 1 per cent. solution of sodium nitrite, a green colour passing through blue to violet indicates the presence of biliary colouring matter. Another test is to add a few drops of hydrogen peroxide to the acetic acid solution when a permanent green coloration is produced. The remainder of the acetic acid solution is evaporated to dryness, and the residue boiled for several minutes with 2 c.c of water and 2 drops of a 25 or 30 per cent. solution of normal potassium oxalate; after filtering and evaporating the filtrate to dryness, the cold residue is mixed with 1 c.c. of alcohol, 1 drop of a sugar solution, and 1 c.c. of sulphuric acid according to Pettenkofer's reaction.

J. J. S.

# INDEX OF AUTHORS' NAMES.

## ABSTRACTS. 1897. Parts I & II.

(Marked A. i and A. ii respectively); and also to Transactions, 1897, (marked T.); and to Proceedings of the Session 1896—1897, Nos. 169 to 182, Nov., 1896—June, 1897 (marked P.).

### A.

C.

## D.

E.

F.

## G.

## I.



## J.

## K.

## L.

M.

## N.

## O.

P.

T.

## U.

# INDEX OF SUBJECTS.

## ABSTRACTS. 1897. Parts I. & II.

(Marked A. i. and A. ii. respectively); and also to Transactions, 1897 (marked T.); and to Proceedings of the Session 1896—1897, Nos. 169 to 182, Nov., 1896—June, 1897 (marked P.).

### INDEXERS.

J. BRUCE.
F. H. CARR.
A. W. CROSSLEY, M.Sc., Ph.D.
T. EWAN, B.Sc., Ph.D.
M. O. FORSTER, Ph.D.
J. S. HALDANE, M.A., M.D., F.R.S.
P. A. E. RICHARDS.
L. J. SPENCER, M.A.
J. F. THORPE, Ph.D.

### A.

## B.

D.

## E.

**F.**

## G.

H.

## I.

J.



K.

## L.

## N

## O.

## P.

## Q.

## U.

## V.

*o-Xylene, Me : Me*=1 : 2 ; *m-xylene, Me : Me*=1 : 3 ; *p-xylene, Me : Me*=1 : 4.

## X.

*o-Xylene, Me* : *Me*=1 : 2; *m-xylene, Me* : *Me*=1 : 3 ; *p-xylene, Me* : *Me*=1 : 4.



## Y.



## Z.

# ERRATA

## Vol. LXXII. (Abstr., 1897).

### Part I.

| Page | Line | |
|---|---|---|
| 89 | 22 | *for* "$CH_2<\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CHPr\cdot CO}>CMe$" *read* "$CH_2<\genfrac{}{}{0pt}{}{CH_2-CH}{CHPr\cdot CO}>CMe$." |
| 100 | 15*, 14* | *for* "isobutyrylphenylhydrazide" *read* "isobutyrylphenylmethylhydrazide." |
| 136 | bottom | ,, "bromide" *read* "bromine." |
| 140 | 4 | ,, "*ethylic γ-chlorisosuccinate*" read "*ethylic γ-chlorethylisosuccinate.*" |
| 140 | 6 & 7 | ,, "ethylamide" *read* "ethylimide." |
| 174 | 6 | ,, "$C_8H_{15}N\cdot O\cdot C_7H_{11}N$" *read* "$C_8H_{14}N\cdot O\cdot C_7H_{11}N$." |
| 216 | 20* | ,, "$C_4H_4$" *read* "$C_4H_9$." |
| 278 | 19 | ,, "$NH_2\cdot C_6H_2(NO_2)<\genfrac{}{}{0pt}{}{-N}{NH}>CMe_2$" *read* "$NH_2\cdot C_6H_2(NO_2)<\genfrac{}{}{0pt}{}{-N}{NH}>CMe$." |
| 282 | 23* | ,, "$(CH_3\cdot CO)_2$" *read* "$(CH_3\cdot CO)_2O$." |
| 284 | 10 | ,, "$NH_2\cdot CO\cdot NH_2\cdot C_6H_4\cdot O\cdot CH_2\cdot COOH$" *read* "$NH_2\cdot CO\cdot NH\cdot C_6H_4\cdot O\cdot CH_2\cdot COOH$." |
| 317 | 19* | ,, "$COPr^{\alpha}\cdot COPr_{\alpha}$" *read* "COEt·COEt." |
| 395 | 4 | ,, "Allythiocarbimide" *read* "Allylthiocarbimide." |
| 476 | 18 | ,, "metanitrobenzoic acid" *read* "metabromobenzoic acid." |
| ,, | 8* and 7* | ,, "1:2:4:6-chlorotribromaniline" *read* "1:2:4:6-chlorotribromobenzene." |
| 440 | 20*, 17* | ,, "ethoxymethyleneacetate" *read* "ethoxymethyleneacetoacetate." |
| 583 | 2* and 1* | *should read* "The absorption spectrum of the green colouring matter shows it is not identical with Petit's physostygmine-blue or with Duquesnel's rubreserine." |
| 616 / 622 | 10 / 6 | *for* "Erhardt" *read* "Ehrhardt." |
| 621 | 9* | ,, "dimethyl" *read* "trimethyl." |
| 647 | 15 | ,, "$C_{14}H_2NO_2$" ,, "$C_{14}H_{25}NO_2$." |

### Part II.

| Page | Line | |
|---|---|---|
| 43 | 11 | *delete* "hydrogen peroxide or." |
| 218 | 21* | *for* "M" *read* "Ni." |
| 268 | 8* | *delete* "artificial." |
| 335 | 14 and 16 | *for* "sardines" *read* "tunny." |
| 458 | bottom | ,, "1897" *read* "1896." |
| 609 | 21 | ,, "Herzig" *read* "Herbig." |

### Index.

| Page | Col. | Line | |
|---|---|---|---|
| 668 | ii | 23 | *for* "the viscosity of miscible liquids" *read* "the viscosity of mixtures of miscible liquids." |
| 754 | i | 9 | ,, "**ψ-Cumenoxyacetyl**" *read* "**ψ-Cumenoxyacetal.**" |
| 793 | ii | 20*-15* | "**Hexadienes**" *should be under* "**Hexinene,**" page 794, col. ii. |

* From bottom.